

activation greatly increased by a hydrogenic environment.

Since the Ba^{134} resulting from the decomposition is not found by mass spectrum analysis, it may be presumed to be unstable. However, we have added a small amount of barium to cesium nitrate activated by neutrons and upon precipitating the barium chemically, have found that the barium shows no activity of half-lives between ten minutes and three days. Chemical separations also show the absence of radio-iodine or radio-xenon.

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**THE REACTION OF FLUORINE WITH NITRIC ACID
AND WITH SOLID POTASSIUM NITRATE TO FORM
 NO_3F**

Sir:

Cady [THIS JOURNAL, 56, 2635 (1934)] has recently discovered that when fluorine is bubbled through 3 *N* nitric acid, the remarkable compound NO_3F is formed. Through Dr. Cady's kindness his apparatus was made available to us and we have repeated the preparation. The resulting material has all the properties described by him. It boils at about -42° , it liberates iodine from iodides and, in the gaseous form, it explodes when heated to some 200 or 300° .

We have found that NO_3F reacts very slowly with VO^{++} to give vanadic acid, and that no appreciable reaction takes place with Mn^{++} in 6 *N* H_2SO_4 , as judged by color changes. When, however, the gas is brought in contact with solutions of silver nitrate, a black precipitate (Ag_2O_3) forms at once. Mixtures of Mn^{++} and Ag^+ in 6 *N* H_2SO_4 reacted with the NO_3F to give permanganate. The reaction with silver ion is convenient for testing purposes if ozone and OF_2 are known to be absent.

We have also found that fluorine reacts readily and efficiently with solid potassium nitrate to form a substance that appears to be NO_3F . The gas explodes on heating, it reacts with iodide ion and silver ion in the manner described above, and the boiling point agrees, qualitatively, with that given by Cady for NO_3F . Twenty cc. of the substance in the liquid state (at -79°) was prepared.

By allowing it to boil at atmospheric pressure for a time it was freed from any of the more volatile impurities. The vapor, at atmospheric pressure, was then passed through dilute nitric acid to remove any hydrolyzable impurities. It was then distilled from a trap cooled to -78° into a trap immersed in liquid air. The resulting material had, when molten, and unlike the material prepared from nitric acid, a very slightly yellowish color. Due to some other substances, or to a slow decomposition, an apparently constant pressure of from 5 to 10 mm. developed above the material cooled with liquid air, even after repeated pumping. The solid material, while under vacuum in the trap cooled with liquid air, eventually exploded very violently (danger!), and for no obvious reason.

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1,2-BENZOPYRENE

Sir:

In preparing a quantity of 1,2-benzopyrene required in a study which is being carried out in collaboration with the Office of Cancer Investigations, U. S. Public Health Service, the synthesis of Cook and Hewett [*J. Chem. Soc.*, 398 (1933)] has been modified to advantage in certain details, the over-all yield from pyrene being 36%.

The condensation of pyrene (0.6 mole) with succinic anhydride (0.72 mole) in nitrobenzene solution (600 cc.) with aluminum chloride (190 g.) was carried out as described [THIS JOURNAL, 54, 4351 (1932)] for the similar condensation of acenaphthene. Sodium β -1-pyrenoylpropionate was collected after one crystallization and washed free of tars with alcohol and ether. The material was directly pure and suitable for reduction; yield 90–94%. The method of reduction of Cook and Hewett was not improved in yield (71–75%, pure), but the process was simplified. After acidifying the solution of γ -1-pyrenylbutyric acid, the suspension was heated at the boiling point for one hour to dehydrate the hydroxy acid and give a granular product. This was extracted with hot sodium bicarbonate solution, then with cold soda solution, and the combined filtrates were acidified and digested. The crude acid (m. p. 181–183°) was crystallized once from xylene (m. p. 187–188°).

For the ring closure, 50 g. of the pure acid was suspended in 0.5 liter of dry ether with 75 cc. of thionyl chloride, and pyridine (3 drops) was added. In one to two hours (25°) the acid had dissolved and the solution, filtered if necessary, was concentrated at the pump with gentle warming. The acid chloride, which soon solidified, was freed of reagent by adding and evaporating portions of ether, breaking the lumps and evacuating. A solution of the gray solid in 0.5 liter of carbon disulfide was cooled in ice and treated with 25 cc. of stannic chloride in 25 cc. of solvent, when the solution slowly deposited a purplish-red complex. After three hours at 0°, the mixture was refluxed for three hours, decomposed with ice and acid and steam distilled. The yellow solid was extracted with glacial acetic acid from some dark tar and precipitated with water. The ketotetrahydrobenzpyrene was bright yellow, m. p. 169–171°, and suitable for further use; yield, 37.5–39.5 g. (80–84%).

The ketone was reduced in yields of only 40–55% with hydrazine and sodium ethylate, through the semicarbazone, or by the Clemmensen method using alcohol, acetic acid or (best) dioxane. The best method was by hydrogenation in alcohol at 200° and 3000 lb. pressure with copper chromite catalyst, the yield of distilled material (m. p. 98–101°) suitable for dehydrogenation being 84%. 1',2',3',4'-Tetrahydro-1,2-benzpyrene crystallizes from alcohol as faintly yellow plates, m. p. 113° (calcd.: C, 93.71; H, 6.30. Found: C, 93.66; H, 6.49); picrate, red needles, m. p. 166° (calcd.: N, 8.66. Found: N, 8.44).

The crude tetrahydride (8 g.) was dehydrogenated with selenium (14 g.), added in 3 portions, at 330° for thirty-six hours. The product was extracted with benzene, distilled (6.8 g., m. p. 168–170°), and crystallized from glacial acetic acid,

giving 5.5 g. of 1,2-benzpyrene, m. p. 176–176.5° and, from the mother liquor, 0.7 g. of material, m. p. 172–173°; yield, 79%. Mixtures of 1,2-benzpyrene and its tetrahydride are not easily separated by crystallization, but such material can be purified with little loss by further treatment with selenium. Our purest material melted at 176.5–177° and the plates from glacial acetic acid rapidly changed to micro needles on standing with cold acetic acid or alcohol. It is possible that the very active 1,2-benzpyrene preparation of Maisin and Liégeois [*Compt. rend. soc. biol.*, **115**, 733 (1934)] contained the tetrahydro compound as an impurity [compare Winterstein and Vetter, *Z. physiol. Chem.*, **230**, 169 (1934)], and the latter substance is being tested. A rapid method of preparing small amounts of 1,2-benzpyrene (m. p. 174–175°) consisted in the pyrolysis of a mixture of the cyclic ketone (2 g.) with zinc dust (50 g.), covered with zinc dust (50 g.).

Two other hydrocarbons which are being tested were prepared by the reaction of ketotetrahydrobenzpyrene in benzene solution with methylmagnesium iodide. This gave directly 4'-methyl-1',2'-dihydro-1,2-benzpyrene. The crude material (m. p. 151–153°, 73% yield) was crystallized from dilute acetic acid; pale yellow plates, m. p. 155–156° (calcd.: C, 93.99; H, 6.01. Found: C, 93.82; H, 6.23). Treatment with selenium at 330° gave 4'-methyl-1,2-benzpyrene: large yellow plates, m. p. 217.5–218°, red-yellow fluorescence in concentrated sulfuric acid (calcd.: C, 94.70; H, 5.30. Found: C, 94.68; H, 5.52). The picrate forms dark purplish-brown needles, m. p. 203–204°, from benzene (calcd.: N, 8.49. Found: N, 8.94).

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