TABLE I

CHROMATOGRAPHIC ANALYSES OF HYDROGEN

Equilibration temp., °K.	Ortho:Para Ratio Found	Calcd.[3]	Fig. 1
~300	3.04 ± 0.15	3.00	A
77.4	0.97 ± 0.05	0.99	B
64	0.66 ± 0.03	0.63	C

as a dilute helium solution, was rechromatographed to check the retention time and purity (Fig. 1, D and E).

With a properly activated column, there is no detectable "irreversible adsorption." When samples of hydrogen were injected slowly between the end of the chromatographic column and the combustion tube using a syringe driven at constant speeds, the areas of the resultant rectangular peaks were the same (± 3%) as the sums of the areas of the ortho- and parahydrogen peaks produced when samples of identical size were injected at the front of the column.

That substantial separation of ortho- and paradeuterium occurs is shown by the shoulder on the trailing edge of the deuterium peak (Fig. 1, F). The peak assignment is based upon the ortho: para ratio of 2.00 for normal deuterium. The deuterium isomers are separated completely from the hydrogen isomers; however, orthohydrogen is eluted only slightly more rapidly than HD.

To aid in the interpretation of these separations, we are in the process of measuring chromatographically the heats of adsorption.

(3) Ref. 2, p. 14.

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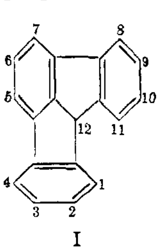
FLUORADENE (INDENO[1,2,3-*jk*]FLUORENE), AN UNUSUALLY ACIDIC HYDROCARBON

Sir:

In continuation of our study of cyclopentindene compounds[1,2] we wish to report the synthesis and some of the properties of fluoradene (indeno [1,2,3-jk]fluorene) (I) [m.p. 129.8-130.3°. *Anal.* Calcd. for $C_{19}H_{12}$: C, 95.0; H, 5.0; mol. wt., 240. Found: C, 94.8; H, 4.9; mol. wt. (Rast) 235], prepared in 23% yield by deamination of IIa.[3] As was anticipated, the presence of two additional fused benzene rings led to a more highly strained system in fluoradene than was present in the parent 2,2a,3,4-tetrahydro-1H-cyclopent[cd]indene.[1] Of particular interest is the unusually strong acidity of the hydrogen on C_{12}.



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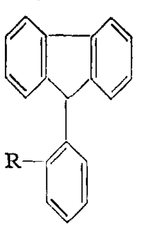
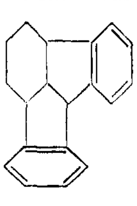


IIa, R = NH_2
IIb, R = OH



III

The structure of fluoradene was established (1) by its method of synthesis, (2) by elementary analyses and molecular weight determinations, and (3) in particular by its ease of hydrogenation and consumption of perbenzoic acid, reactions which are characteristic for such strained, fused ring compounds.[1,2] The hexahydrofluoradene (III) [m.p. 118.4–119.4. *Anal.* Calcd. for $C_{19}H_{18}$: C, 92.6; H, 7.4. Found: C, 92.5; H, 7.2] resulted from a rapid 300 mole % hydrogen absorption in methanol at room temperature in the presence of palladized carbon. Its ultraviolet spectrum was that of two 1,2- or 1,3-dialkylindanes,[4] and this lends strong support to the structural assignment. At room temperature, fluoradene (I) consumed 400 mole % of perbenzoic acid while under the same conditions 9-phenylfluorene consumed 50 mole %. Both of these reactions reflect the presence of appreciable strain in the benzene ring which is doubly-fused to five-membered rings.

The most unusual property of fluoradene is the acidity of the one remaining non-aromatic hydrogen at C_{12}. This was first observed when it was discovered that fluoradene could be removed from benzene by washing with dilute aqueous alkali and was confirmed by exchanging this hydrogen for deuterium in boiling deuterium ethoxide, conditions under which 9-phenylfluorene shows no exchange. In alkaline solution fluoradene develops a pink color reminiscent of phenolphthalein. On acidification, fluoradene is recovered, but in the presence of oxygen the color fades and 12,12′-bifluoradenyl is formed [m.p. 306–307 dec. *Anal.* Calcd. for $C_{38}H_{22}$: C, 95.4; H, 4.6. Found: C, 95.4; H, 4.7.], identical with the product from the reaction of 12-bromofluoradene with mercury. To obtain a quantitative measure of this acidity, the distribution of fluoradene was examined between hexane and 97% aqueous methanol as a function of pH. By this procedure, a pK'_a of 11 ± 0.5 (extrapolated to water) was found for fluoradene.[5] This is a truly remarkable acidity and should be compared with the most acidic hydrocarbons heretofore known, 9-phenylfluorene, phenylacetylene, and indene,[6] for which pK_a''s of 21 or greater have been reported. Undoubtedly, the high symmetry and complete conjugation in the fluoradene anion are responsible for this extreme acidity.

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

(2) H. Rapoport and G. Smolinsky, *ibid.*, **79**, 5831 (1957).

(3) It is of interest to note that a recent attempt to prepare I from 9-(*o*-aminophenyl)-9-fluorenol by deamination led to tribenzotropone as the only product in addition to the phenol [M. Stiles and A. J. Libbey, Jr., *J. Org. Chem.*, **22**, 1243 (1957)].

(4) J. Entel, C. H. Ruof and H. C. Howard, *Anal. Chem.*, **25**, 1303 (1953).

(5) The same method applied to 9-(*o*-hydroxyphenyl)-fluorene (IIb) led to a pK_a' of 12.2 in 97% aqueous methanol. In water, this phenol has a pK_a' of 9.7, and the difference, 2.5 pK units, was used for the extrapolation of fluoradene's acidity to water.

(6) J. B. Conant and G. W. Wheland, THIS JOURNAL, **54**, 1212 (1932); W. K. McEwen, *ibid.*, **58**, 1124 (1936).