no detectable quantities of IV. The deuterium-labeling experiments *and the total absence of IV from the irradiation of I* provide strong support for mechanism B. Although we are unaware of any close analogy, recent work by Leermakers on the photolysis of pyruvic acid bears similar characteristics.[10] The reaction has been proposed to involve an n–π^* state which proceeds *via* an uncommon five-membered transition state.

The nature of the excited state responsible for the photoreaction remains somewhat questionable at this time, although in the present instance the benzoyl group is involved, and the lowest triplet configuration of such a moiety is n–π^*. Appropriate quenching experiments with added piperylene (3 *M*) or cyclohexadiene demonstrated that the over-all process was unaffected by these triplet quenchers. This is indicative of reaction from an upper singlet state or from a triplet manifold at a rate exceeding diffusional control.

Of the various mechanisms considered for the photoisomerization of cyclopropyl[11] and appropriate α,β-epoxy ketones,[12] it is perhaps surprising that an internal 1,5-H transfer sequence has not been considered. Further work both on the mechanism of the rearrangement and on the scope and application to other small ring systems is currently under way and will be the subject of future reports.

Acknowledgment. The authors are indebted to the Public Health Service (Grant GM 13990-01) for generous support of this research.

(10) P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85**, 3776 (1963).
(11) J. N. Pitts and I. Norman, *ibid.*, **76**, 4815 (1954).
(12) O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964).

Albert Padwa, William Eisenhardt
Department of Chemistry
State University of New York at Buffalo
Buffalo, New York 14214
Received January 27, 1968

Acidity of Hydrocarbons. XXIX. Kinetic Acidities of Benzal Fluoride and 9-Fluorofluorene. A Pyramidal Benzyl Anion[1]

Sir:

Large and often contrasting effects of fluorine substituents have been interpreted frequently in terms of an electron-attracting inductive field effect and an electron-donating mesomeric effect. When the latter effect involves conjugation of an electron-rich fluorine p orbital with an electron-rich π system, the result is a destabilization.[2] We wish to report a striking example of the operation of these contrasting effects in the kinetic acidities of α,α-difluorotoluene and 9-fluorofluorene.

α,α-Difluorotoluene was prepared by the reaction of benzaldehyde with sulfur tetrafluoride in an autoclave at 190° for 12 hr. The product, bp 64–65° (66 torr), was identified by nmr (multiplet at δ 6.5–7.0 (5 H), triplet at 5.90 ppm, J_{H-F} = 56 cps) and analysis. The α-deuterated and -tritiated material was prepared similarly. The compound is not stable toward lithium cyclohexylamide (LiCHA) in cyclohexylamine; presumably the conjugate anion eliminates fluoride ion to form a carbene. This process results in neutralization of the base catalyst. Relative exchange rates were obtained by comparing the loss of deuterium and tritium in undecomposed substrate with that of a standard, fluorobenzene-2-*d*(*t*) or 1,3-difluorobenzene-4-*t*, also present.[3] In cyclohexylamine at 25° toward LiCHA, relative rates, $k(\alpha,\alpha$-difluorotoluene$)/k($*o*-fluorobenzene), are D, 5.30 ± 0.23, and T, 4.41 ± 0.11. Since the previously determined rate of *o*-fluorobenzene relative to α-toluene is D, 2400, and T, 2250,[3] the corresponding α,α-difluorotoluene/toluene ratios are D, 1.3×10^4, and T, 1.0×10^4, and the isotope effect is k_D/k_T = 2.9. In a similar kinetic run with 1,3-difluorobenzene-4-*t*, we find the relative rates, $k(\alpha,\alpha$-difluorotoluene$)/k($*o*,*p*-difluorobenzene), are D, 0.68, T, 0.71, and k_D/k_T = 2.8. The relative reactivity of the *o*,*p*-difluorobenzene system has not yet been determined directly, but by assuming the constancy of the partial rate factors in ref 3 we obtain an indirect measure of $k(\alpha,\alpha$-difluorotoluene$)/k$(toluene) for D, 1.8×10^4, and T, 1.5×10^4. Agreement between the two runs is reasonable considering the additional assumption required.

9-Fluorofluorene was prepared by stirring 9-bromofluorene with dry silver fluoride in acetonitrile at room temperature for 30 min. The reaction mixture was diluted with water and extracted with pentane. After removing the pentane by vacuum evaporation the product was crystallized from methanol at −60°, mp 60–60.5°. The ir spectrum showed a strong C–F band at 1000 cm^{-1}, the mass spectrum gave a molecular weight of 184, and the uv spectrum was normal for a fluorene derivative (λ_{max} 222, 238, 246, 258, 275 mμ). The nmr spectrum gave a multiplet at δ 6.70–7.70 ppm (8 H) and a doublet centered at δ 5.91 ppm (1 H); J_{H-F} = 53.5 cps was independent of field strength (60 and 100 MHz). The compound is unstable at room temperature and decomposes rapidly to polymers and HF. A methanol solution was found to be stable. 9-Fluorofluorene-9-*d*(*t*), mp 60–61.5°, was prepared in the same way from 9-bromofluorene-9-*d*(*t*). With sodium methoxide in methanol, isotope exchange is much faster than loss of fluoride, and simple pseudo-first-order kinetics was obtained. At 45°, $k_D = 11 \times 10^{-5}\ M^{-1}\ sec^{-1}$, $k_T = 6.0 \times 10^{-4}\ M^{-1}\ sec^{-1}$, and k_D/k_T = 1.9. The rates relative to fluorene are D, 0.12, and T, 0.14.[4,5]

The sodium methoxide catalyzed isotope exchange of fluorene is *reduced* by a factor of eight by a 9-fluoro substituent. This effect is clearly a manifestation of conjugative destabilization; 9-chloro- and 9-bromofluorenes are 4×10^2 and 7×10^2, respectively, more reactive than fluorene.[5] From the correlation of inductive substituents in the 9 position with σ_I or its

(1) (a) Supported in part by Grant No. GM-12855 of the National Institutes of Health, U. S. Public Health Service. (b) Paper XXVIII: A. Streitwieser, Jr., J. A. Hudson, and F. Mares, *J. Am. Chem. Soc.*, **90**, 648 (1968).
(2) J. Hine, L. G. Mahone, and C. L. Liotta, *ibid.*, **89**, 5911 (1967), have reviewed the destabilizing effect of fluorine in conjugated anions but have attributed the effect to a C–F σ-bond energy change resulting from the increased electronegativity of sp^2 compared to sp^3 carbon. This interpretation parallels the π-electron energy explanation for many cases, but a clear distinction should soon be possible from quantum chemical calculations.
(3) This technique is described in detail in A. Streitwieser, Jr., and F. Mares, *J. Am. Chem. Soc.*, **90**, 644 (1968).
(4) A. Streitwieser, Jr., A. P. Marchand, and A. H. Pudjaatmaka, *ibid.*, **89**, 693 (1967).
(5) A. H. Pudjaatmaka, unpublished results.

equivalent[4] and $\sigma_I = 0.5$ for fluorine, we calculate that the inductive effect alone of a 9 fluorine would result in a rate increase of 10^5; hence, the π-conjugation effect actually results in a millionfold rate decrease.

By contrast, two α fluorines *increase* the LiCHA-catalyzed exchange of toluene by a factor of $>10^4$.[6] The relatively high primary isotope effects obtained for both systems ensure that the rates measured are those of hydrogen abstraction; that is, internal return is not important in either case. To explain these apparently divergent results we propose that the 9-fluorofluorenyl anion is *planar* whereas the α,α-difluorobenzyl anion is *pyramidal*. Estimates of the magnitude of the inductive stabilization of a nonconjugating pyramidal phenyldifluoromethyl anion are fully consistent with the observed reactivity of benzal fluoride. For this system the increased conjugation of a planar benzyl anion is countered by the corresponding increased conjugative destabilization of the two fluorines that are then also coplanar. However, the stability associated with a planar fluorenyl anion is much greater than for a phenyl anion and overcomes the destabilizing effect of a single conjugating fluorine.

These results may be generalized into the following working hypothesis: *a fluorine substituent stabilizes a pyramidal or nonconjugated anion but can destabilize a conjugated anion.* Such obvious corrolaries that trifluoromethyl anion is pyramidal and that nitrogen trifluoride should have a smaller bond angle than ammonia, etc., will be developed in the full paper. Similar considerations apply in a direct way to oxygen and nitrogen substituents.

(6) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press Inc., New York, N. Y., 1965, p 59, reports that all four hydrogens of *m*-methylbenzal fluoride undergo hydrogen–deuterium exchange at comparable rates with potassium *t*-butoxide in *t*-butyl alcohol-*d*. This corresponds to a far slower relative rate for the difluoromethyl hydrogen than we have found, but this apparent discrepancy may very well be due to extensive internal return in the *t*-butyl alcohol system.

(7) On leave from the Institute of Chemical Process Fundamentals, Prague, Czechoslovakia.

A. Streitwieser, Jr., F. Mares[7]
Department of Chemistry, University of California
Berkeley, California 94720
Received January 27, 1968

Alkaloid Studies. LIX.[1] The Structure and Absolute Configuration of Vallesamidine

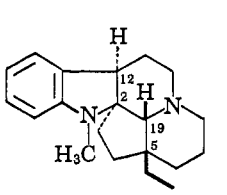
Sir:

In 1965 we reported[2] the isolation of 28 alkaloids from *Vallesia dichotoma* Ruiz *et* Pav. One of these appeared to be isomeric with N-methylaspidospermidine (II) on the basis of physical and chemical data, but no definite structure could be assigned in view of the very limited amount of material. We report now the determination of the molecular structure and absolute configuration of this new alkaloid, vallesamidine (I), by X-ray diffraction analysis. Formally, vallesamidine (I) differs from the usual aspidospermine skeleton (*e.g.*, III) only in that C-19 is attached to the indole nucleus at C-2 rather than at C-12.

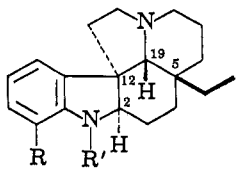
(1) For paper LVIII see R. R. Arndt, S. H. Brown, N. C. Ling, P. Roller, C. Djerassi, J. M. Ferreira, B. Gilbert, E. C. Miranda, S. E. Flores, A. P. Duarte, and E. P. Carrazzoni, *Phytochemistry*, **6**, 1653 (1967).

(2) A. Walser and C. Djerassi, *Helv. Chim. Acta*, **48**, 391 (1965).

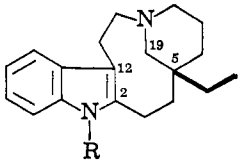
This is the first direct determination of the absolute configuration of a naturally occurring alkaloid related to aspidospermine (III). As such it lends support to the previous conclusions[3,4] regarding absolute configurations in the *Aspidosperma* alkaloid series. Alkaloids of this group isolated[2] in common with vallesamidine (I) include (+)-N-methylaspidospermidine (II), (−)-aspidospermine (III), (−)-vallesine (IV), (−)-N-methylquebrachamine (V), and (+)-haplocidine. By means of the optical rotatory dispersion technique[3] and chemical interconversions[2,4–6] these compounds have been shown to have the same absolute configurations at their respective equivalent asymmetric centers (carbons 2, 5, 12, and 19 in II). Stereochemically, vallesamidine (I) belongs to the same class, and it is particularly noteworthy that the absolute configuration at carbon 5 in I is the same as that at the equivalent carbon (5 in II–V) in all of the co-occurring aspidospermine-type bases for which the absolute configuration is known.



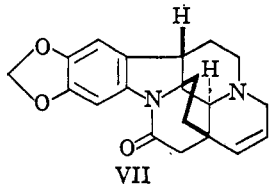
I



II, R = H; R′ = CH_3
III, R = OCH_3; R′ = CH_3CO
IV, R = OCH_3; R′ = CHO



V, R = CH_3
VI, R = H



VII

Camerman, *et al.*,[4] have shown that the aspidospermine skeleton (II–IV), with correct relative stereochemistry, can be generated by the intramolecular cyclization of quebrachamine (VI), the stereochemistry at carbon 5 determining the configuration at the other three asymmetric centers formed. This observation supports the earlier suggestion[7] that the path to the *Aspidosperma* alkaloids (II–IV) *in vivo* proceeds *via* quebrachamine-like intermediates (V, VI). Vallesamidine (I) might be regarded as the product of an "abnormal" cyclization which, however, generates the same stereochemistry at carbons 2, 12, and 19 as in the "normal" case. Such a biosynthetic route

(3) W. Klyne, R. J. Swan, B. W. Bycroft, D. Schumann, and H. Schmid, *Helv. Chim. Acta*, **48**, 443 (1965).

(4) A. Camerman, N. Camerman, J. P. Kutney, E. Piers, and J. Trotter, *Tetrahedron Letters*, 637 (1965); J. P. Kutney and E. Piers, *J. Am. Chem. Soc.*, **86**, 953 (1964).

(5) K. Biemann and G. Spiteller, *Tetrahedron Letters*, 299 (1961); K. Biemann, M. Spiteller-Friedmann, and G. Spiteller, *J. Am. Chem. Soc.*, **85**, 631 (1963).

(6) G. F. Smith and M. A. Wahid, *J. Chem. Soc.*, 4002 (1963).

(7) C. Djerassi, A. A. P. G. Archer, T. George, B. Gilbert, and L. D. Antonaccio, *Tetrahedron*, **16**, 212 (1961); E. Wenkert, *J. Am. Chem. Soc.* **84**, 98 (1962); K. Biemann, M. Spiteller-Friedmann, and G. Spiteller, *Tetrahedron Letters*, 485 (1961).