**Table II.** Nucleophilic Reactivity Constants toward Methyl Iodide

| Nucleophile | $n_{CH_3I}$[a] |
|---|---|
| $CH_3OH$ | 0.00 |
| $Cl^-$ | 4.37 |
| $NH_3$ | 5.50 |
| $Br^-$ | 5.79 |
| $I^-$ | 7.42 |
| $(n\text{-}C_4H_9)_3P$ | 8.69 |
| $S_2O_3^{2-}$ | 8.95 |
| $(C_6H_5)_3Sn^-$ | ~11.5 |
| $(C_6H_5)_3Ge^-$ | ~12 |
| $Cobaloxime_s \cdot P(n\text{-}C_4H_9)_3$ | 13.3 |
| $Cobaloxime_s \cdot pyridine$ | 13.8[b] |
| $Cobaloxime_s$ (aqua) | 14.3[b] |
| Vitamin $B_{12s}$ | 14.4 |

[a] Except for the last four entries, data taken from ref 8. [b] Calculated from relative rates of reaction with *n*-propyl chloride.

addition of methyl iodide to such a mixture produces methylcobalamin.[10] To obtain further information on the position of the equilibria in eq 1, the stability of vitamin $B_{12s}$ was determined as a function of pH. In the presence of 1 atm of hydrogen gas and a platinum catalyst, vitamin $B_{12s}$ is stable *only above pH ~9.9*. At lower pH values, decomposition into vitamin $B_{12r}$ and hydrogen takes place.[11] Vitamin $B_{12r}$ and hydrogen (1 atm) in the presence of a platinum catalyst similarly proved unstable above pH 9.9, readily forming vitamin $B_{12s}$. In the absence of a catalyst the equilibrium between vitamin $B_{12s}$ and vitamin $B_{12r} + H_2$ is achieved only slowly. For this reason it is possible to generate vitamin $B_{12s}$ below pH 9.9 at higher than equilibrium concentrations. With metallic zinc or chromous ion as the reducing agents, the reduction is even possible in mildly acidic medium (*e.g.*, acetate buffer). The resulting solutions of vitamin $B_{12s}$ are metastable under these conditions, however, and decompose into hydrogen and vitamin $B_{12r}$; we have observed that the decomposition proceeds much more rapidly upon the addition of a platinum catalyst.

Assuming that $[Co^I] \approx [Co^{II}]$ at the observed equivalence point (pH 9.9, at 1 atm of $H_2$), the standard reduction potential of the $B_{12r}$–$B_{12s}$ couple must be approximately −0.59 V. From this estimate the equilibrium constant for the reaction

$$(Co^I) + H^+ \underset{}{\overset{Pt,\ H_2O}{\rightleftharpoons}} (Co^{II}) + 0.5H_2 \qquad (4)$$

is calculated to be of the order of $10^{-10}$ atm$^{1/2}$ $M^{-1}$. Therefore, at pH 7, only about 0.1% of the vitamin $B_{12}$ could be present as Co(I) (1 atm of $H_2$). However, in view of its high nucleophilicity, this amount of $B_{12s}$ is sufficient to permit alkylation of the cobalt. Thus, when a $10^{-3}$ *M* solution of vitamin $B_{12r}$ (which does not react with alkylating agents) is buffered at pH 7 and shaken with methyl iodide and a platinum catalyst under an atmosphere of pure hydrogen, the formation of methylcobalamin is complete after 2 hr of shaking (the rate-determining step in this reaction involves a reaction at the surface of the platinum catalyst).

The similarly high values of the nucleophilicities of various $cobaloxime_s$ derivatives, in comparison with vitamin $B_{12s}$, are in line with other vitamin $B_{12}$-like chemical properties of these compounds.[12] The experiments with the cobaloximes show that the nucleophilicity of $cobaloxime_s$ depends on the nature of the axial base component. This is expected in view of the effect of axial coordination upon the charge density on the cobalt atom. A detailed study of this effect in vitamin $B_{12s}$ (and other Co(I) chelates) is underway.

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(10) D. H. Dolphin and A. W. Johnson, *J. Chem. Soc.*, 2174 (1965).
(11) Decomposition into $B_{12r}$ and hydrogen also occurs at higher pH if no hydrogen is present (also see ref 2).
(12) See G. N. Schrauzer, *Accounts Chem. Res.*, **1**, 97 (1968), and references therein.
(13) National Institutes of Health Postdoctoral Fellow, 1967–1968 (Contract No. 7-F2-6M-29, 156-01A1).

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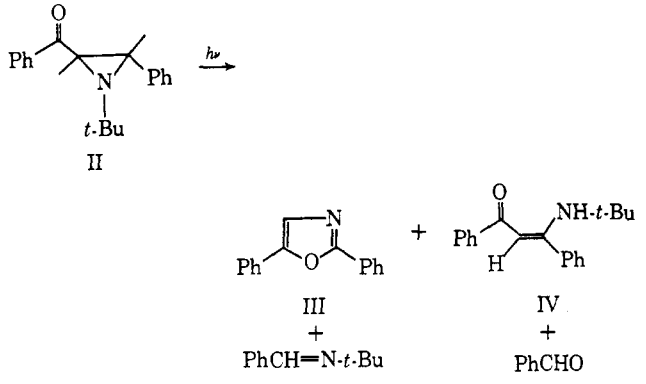
## Evidence for a 1,5-Hydrogen Transfer in the Photochemistry of an Aroylaziridine[1]

*Sir:*

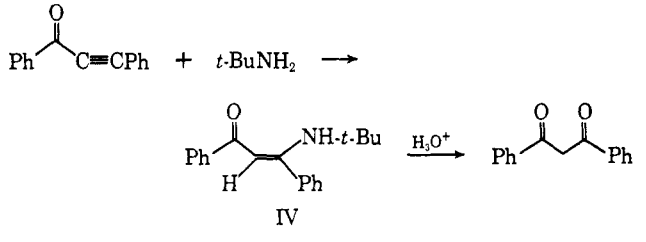
The molecular changes involved in the photochemistry of the 1-benzyl-2-phenyl-3-benzoylaziridine system have been shown to be markedly dependent on the initial stereochemistry.[2] To account for the products obtained from the *trans* isomer we suggested that the reaction proceeds by intramolecular hydrogen transfer from the benzyl carbon to the $p_y$ orbital of oxygen of the $n$–$\pi^*$ excited state. In contrast to the above scheme, irradiation of the *cis* isomer gave products derived from fission of the carbon–carbon bond of the heterocyclic ring. Because such strikingly different photobehavior was observed, a more thorough investigation of N-substituted 2-phenyl-3-benzoylaziridines seemed desirable. In particular, it was of interest to inspect the photochemistry of a related aziridine system in which the group attached to the nitrogen atom is devoid of $\alpha$ hydrogens. To this end *cis*- and *trans*-1-*t*-butyl-2-phenyl-3-benzoylaziridines (I and II) were studied.

The necessary syntheses were accomplished by treating a mixture of *trans*-benzalacetophenone and *t*-butylamine with iodine in ether.[3] Fractional crystallization gave I, mp 106–107°, and II, mp 69–70°. Spectral data and elemental analyses were in complete agreement with the structures.[4] Irradiation of the *trans* isomer II in moist pentane with a Pyrex filter gave a mixture of four components which could be separated by liquid–liquid partition chromatography. The two major products were identified as 2,5-diphenyloxazole (III) (38%) and (β-*t*-butylamino)-*trans*-benzalacetophenone (IV) (41%), mp 114–115°. The two minor components were shown to be N-*t*-butylbenzalimine (6%) and benzaldehyde (4%).

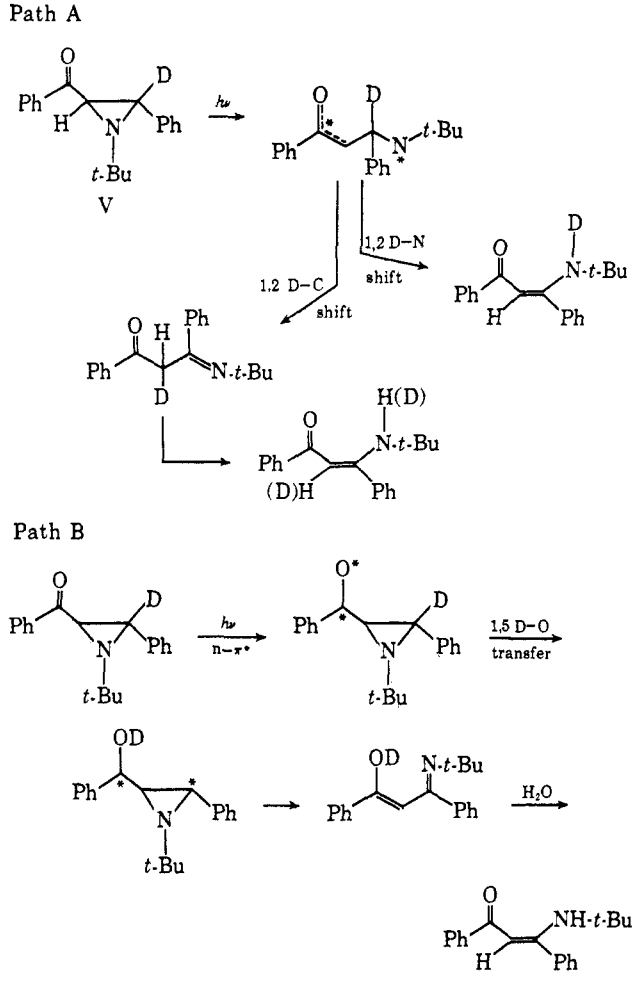
(1) Photochemical Transformations of Small Ring Carbonyl Compounds. XVII. For part XVI, see A. Padwa and E. Alexander, *J. Am. Chem. Soc.*, **89**, 6376 (1967).
(2) A. Padwa and L. Hamilton, *ibid.*, **89**, 102 (1967); **87**, 1821 (1965).
(3) P. L. Southwick and D. R. Christman, *ibid.*, **74**, 1886 (1952).
(4) All compounds analyzed satisfactorily. Complete synthetic and degradative details will be given in our full publication.



The structure of the enamine IV is inferred from its composition, spectral data, and chemical behavior. The infrared spectrum of IV was characterized by bands at 6.30, 7.51, 8.38, and 13.01 $\mu$. The ultraviolet spectrum in 95% ethanol has maxima at 243 and 352 m$\mu$ ($\epsilon$ 10,200 and 23,900). The nmr spectrum in deuteriochloroform exhibits a singlet at $\tau$ −1.66, a multiplet centered at $\tau$ 2.42, a singlet at $\tau$ 4.46, and a singlet at $\tau$ 8.81. The peak areas are in the ratio of 1:10:1:9. The fact that the chemical shift associated with the proton attached to the nitrogen is markedly deshielded and is invariant with concentration strongly suggests that the *t*-butylamino group of IV is *cis* to the benzoyl group. Chemical confirmation was obtained by hydrolysis of IV to dibenzoylmethane. Structure IV was further verified by an independent synthesis from phenylbenzoylacetylene and *t*-butylamine.



The mechanism by which II undergoes rearrangement to IV and the identification of the excited state responsible for the reaction are of considerable interest. Two fundamentally different mechanisms seemed possible and are presented in Chart I. Path A involves C–N ring opening followed by a 1,2-H shift. This route bears a strong similarity to the photochemical interconversions of various substituted cyclopropanes and propenes in solution.[5,6] The alternate path (B) involves a prior 1,5-hydrogen transfer and subsequent ring opening. In order to help elucidate the correct pathway, the photoisomerization of an appropriately deuterium-labeled aziridine was examined. The aroylaziridine chosen for this study was *trans*-1-*t*-butyl-2-phenyl-3-benzoylaziridine-2-$d_1$ (V).[4] Irradiation of V afforded product IV (11%) that was shown to have lost better than 98% deuterium, as evidenced by nmr analysis. The isolation of nondeuterated IV conclusively proves that a 1,2 H–C shift is not operative in path A since a normal deuterium isotope effect would



be expected to give rise to a substantial amount of deuterium on the $\alpha$-carbon atom. Control experiments demonstrated that no exchange of product IV occurred under comparable photolytic conditions, thus negating a 1,2 H–N shift. These results imply that deuterium loss occurs before the formation of the final product and is perfectly consistent with route B.

The quantum yield for appearance of IV from V is 0.006, one-third the value obtained from II.[7] The deuterium isotope effect observed is difficult to rationalize on the basis of mechanism A unless the 1,2-H shift were the slow step. If this were the case, a significant amount of ring opening followed by rotation and closing should occur prior to hydrogen migration and thus allow for the formation of the thermodynamically more stable *cis*-aziridine I.[9] Experimentally, it was found that on short irradiations recovery of aziridine gave only the stereoisomer used as reactant. Deuterium substitution at the 2 position of the aziridine ring also reduced the rate of disappearance of starting material. Thus, irradiation of an equimolar mixture of II and V followed by recovery of the aroylaziridine demonstrated that II disappeared twice as fast as did V. Finally, irradiation of *cis*-aziridine I produced only oxazole III (51%) and *t*-butylbenzalimine (32%) with

(5) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Close, *J. Am. Chem. Soc.*, 87, 1410 (1965); H. Kristinsson and G. W. Griffin, *ibid.*, 88, 378 (1966); G. W. Griffin, A. F. Marcantonio, H. Kristinsson, R. C. Petterson, and C. S. Irving, *Tetrahedron Letters*, 2951 (1965).

(6) A. Padwa in "Organic Photochemistry," Vol. I, O. L. Chapman, Ed., Marcel Dekker, Inc., New York, N. Y., 1967, p 92.

(7) The diminished rate of formation of IV from V implies that the hydrogen-transfer step is not reversible as had been observed in the valerophenone system.[8] This is reasonable in light of the driving force for ring opening of the initial biradical intermediate.

(8) P. J. Wagner, *J. Am. Chem. Soc.*, 89, 5898 (1967).

(9) A. Pohland, R. C. Badger, and N. H. Cromwell, *Tetrahedron Letters*, 4369 (1965).

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–$\pi^*$ 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–$\pi^*$. 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 $\alpha,\beta$-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).

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## 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 $\pi$ 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 $\alpha,\alpha$-difluorotoluene and 9-fluorofluorene.

$\alpha,\alpha$-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 $\delta$ 6.5–7.0 (5 H), triplet at 5.90 ppm, $J_{H-F}$ = 56 cps) and analysis. The $\alpha$-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 $\alpha$-toluene is D, 2400, and T, 2250,[3] the corresponding $\alpha,\alpha$-difluorotoluene/toluene ratios are D, $1.3 \times 10^4$, and T, $1.0 \times 10^4$, 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, $1.8 \times 10^4$, and T, $1.5 \times 10^4$. 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 ($\lambda_{max}$ 222, 238, 246, 258, 275 m$\mu$). The nmr spectrum gave a multiplet at $\delta$ 6.70–7.70 ppm (8 H) and a doublet centered at $\delta$ 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 $4 \times 10^2$ and $7 \times 10^2$, respectively, more reactive than fluorene.[5] From the correlation of inductive substituents in the 9 position with $\sigma_I$ 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 $\sigma$-bond energy change resulting from the increased electronegativity of $sp^2$ compared to $sp^3$ carbon. This interpretation parallels the $\pi$-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.