Table I. Thermodynamics of Protonation and Hydrogen Bonding for Substituted Pyridines and Phosphoroxy Compounds

	Compound	$\Delta\overline{H}_{s(CCl_4)}$, kcal/mol	$-\Delta\overline{H}_{s(HSO_3F)}$, kcal/mol	$-\Delta H_f$,[a] kcal/mol	$-\Delta H_f$,[b] kcal/mol
(1)	Phosphoroxy chloride	$+0.39 \pm 0.03$	4.4 ± 0.1	3.71 ± 0.08	
(2)	Dichlorophenylphosphine oxide	$+0.84 \pm 0.03$	9.9 ± 0.3	4.59 ± 0.08	
(3)	Diethyl chlorophosphate	$+0.77 \pm 0.02$	14.7 ± 0.3	5.55 ± 0.07	
(4)	Trimethyl phosphate	$+0.76 \pm 0.03$	19.6 ± 0.1	6.44 ± 0.09	6.5 ± 0.1
(5)	Triethyl phosphate	$+0.02 \pm 0.05$	20.6 ± 0.2	6.59 ± 0.09	6.5 ± 0.1
(6)	Triphenylphosphine oxide	$+4.15 \pm 0.23$[c]	18.8 ± 0.2[c]		7.4 ± 0.1[d]
(7)	Diethyl ethylphosphonate	-0.64 ± 0.09	23.6 ± 0.3	7.46 ± 0.12	
(8)	Trimethylphosphine oxide	$+5.23 \pm 0.09$	27.0 ± 0.6		7.7 ± 0.2
(9)	3,5-Dichloropyridine	$+4.28 \pm 0.06$	26.4 ± 0.3		5.4 ± 0.3
(10)	2-Bromopyridine	$+0.96 \pm 0.03$	29.2 ± 0.3	5.83 ± 0.09	
(11)	2-Chloropyridine	$+0.96 \pm 0.04$	30.7 ± 0.3	5.93 ± 0.07	
(12)	3-Bromopyridine	$+0.23 \pm 0.03$[d]	34.4 ± 0.3[c]		6.2 ± 0.2[d]
(13)	Quinoline	$+0.46 \pm 0.01$[d]	36.5 ± 0.2	7.47 ± 0.09[d]	7.35 ± 0.1[d]
(14)	Pyridine	$+0.36 \pm 0.02$[d]	38.2 ± 0.2[c]	7.40 ± 0.09[d]	7.1 ± 0.1[d]
(15)	4-Methylpyridine	-0.05 ± 0.01[d]	39.1 ± 0.3	7.59 ± 0.08[d]	7.3 ± 0.1[d]
(16)	2,6-Dimethylpyridine	-0.26 ± 0.06	41.0 ± 0.2[c]	8.44 ± 0.11	7.8 ± 0.3
(17)	2,4,6-Trimethylpyridine	-0.23 ± 0.03	42.9 ± 0.2	8.36 ± 0.12	7.9 ± 0.1

[a] These values were determined using method II, described in ref 4a. [b] These values were determined using method I, described in ref 4a, and where available are the values plotted as $-\Delta H_f$ in Figure 1. Other data plotted in Figure 1 were determined by use of method II. [c] Reference 5a. [d] Reference 4a.

represents a test of the relationship between hydrogen bonding and proton transfer through two well-established thermodynamic procedures and so is probably on solid experimental ground.

The results listed in Table I and portrayed in Figure 1 may be interpreted in at least two ways: (1) that there is a fundamental difference in the way pyridines and phosphoroxy compounds respond as hydrogen bond acceptors in carbon tetrachloride and as proton acceptors in fluorosulfuric acid; and (2) alternatively, the difference between the two series could be assigned to specific differences in the ability of fluorosulfuric acid to solvate pyridinium as compared to phosphoroxonium ions.

Evidence against the second explanation comes from two sources, the first of which being an extensive survey of a number of different types of compounds which gave a close correlation between pK_a and ΔH_i in fluorosulfuric acid. Deviations from this correlation were generally less than 2 kcal/mol even though the correlation covered nearly 50 kcal/mol in terms of each thermodynamic property.[5a] It would require a discrepancy of nearly 15 kcal/mol in ΔH_i in order to superimpose the two correlation lines portrayed in Figure 1. This would seem to be an unreasonably large and specific solvation difference. Secondly, Taft has reported exactly the same type of dispersal of correlation lines for different functional groups in an attempted free energy correlation between the free energy of hydrogen bonding, H, and the pK_a's for the same compounds in water.[4c] Further evidence for the consistency of our data is provided by the fact that ΔH_f for most of the hydrogen bond acceptors shown in Figure 1 gave excellent agreement when determined by the two techniques reported in ref 4a; *i.e.*, formation of a 1:1 complex with PFP at high dilution in carbon tetrachloride or by the injection of solid PFP into the hydrogen bond acceptor serving both as base and solvent. If the two different types of compounds suffered drastically different medium effects in their hydrogen bond formation with PFP, we would expect it to show up in large differences between ΔH_f as determined by the two methods.

We conclude that there are not important differential solvation factors for different families in fluorosulfuric acid or carbon tetrachloride and accordingly that most of the dispersal shown in Figure 1 and in Taft's work[4c,7] arises from different responses of different classes of bases to the two processes, proton transfer and hydrogen bonding. In view of the importance of acid catalysis and hydrogen bonding to phosphoroxy and heterocyclic bases, it is important to realize that various criteria of "basicity" may mean entirely different things in these two series of compounds and probably many others.

(7) H. B. Yang and R. W. Taft, *J. Amer. Chem. Soc.*, **93**, 1310 (1971).

(8) NSF Trainee.

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Flash Photolysis of *N*-Chloroacetyl-*m*-tyramine

Sir:

A common feature of the mechanism underlying the novel photocyclization reactions of *N*-chloroacetylphenethylamines[1] appears to be homolytic or heterolytic cleavage of the C–Cl bond. On the basis of studies on fluorescence quenching[2] and solvent effects a dualistic mechanism has been proposed.[3] In water and protic solvents there is *intramolecular electron transfer* from the excited aromatic chromophore, while in most organic solvents *energy transfer* becomes intramolecular. In aqueous systems photoionization of the electron-donating aromatic nucleus[4] may precede electron scavenging by the chlorinated amide.[5]

(1) O. Yonemitsu, Y. Okuno, Y. Kanaoka, and B. Witkop, *J. Amer. Chem. Soc.*, **92**, 5686 (1970); O. Yonemitsu, H. Nakai, Y. Kanaoka, I. L. Karle, and B. Witkop, *ibid.*, **92**, 5691 (1970).

(2) T. McCall, G. S. Hammond, O. Yonemitsu, and B. Witkop, *ibid.*, **92**, 6991 (1970).

(3) O. Yonemitsu, H. Nakai, Y. Okuno, S. Naruto, K. Hemmi, and B. Witkop, *Photochem. Photobiol.*, in press.

(4) (a) L. I. Grossweiner and H. I. Joschek, *Advan. Chem. Ser.*, No. **50**, 279 (1965); (b) H. I. Joschek and L. I. Grossweiner, *J. Amer. Chem. Soc.*, **88**, 3261 (1966); (c) Yu. A. Vladimirov, D. I. Roshchupkin, and E. E. Fesenko, *Photochem. Photobiol.*, **11**, 227 (1970).

(5) P. B. Ayscough, R. G. Collins, and F. S. Dainton, *Nature (London)*, **205**, 965 (1965); A. Meybeck and J. J. Windle, *Photochem. Photobiol.*, **10**, 1 (1969).

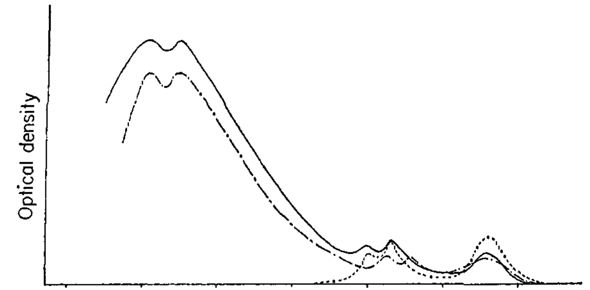
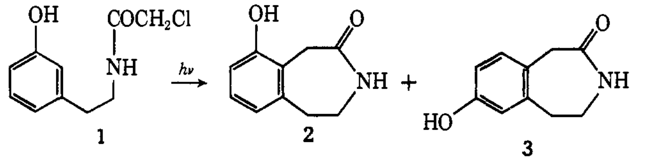


Figure 1. A transient absorption spectrum obtained with a delay time of 5 μsec by the flash photolysis of *N*-chloroacetyl-*m*-tyramine (**1**) in water is shown by a solid curve, in aqueous solution at pH 12.4 by a dashed-dotted curve, and that of *N*-acetyl-*m*-tyramine (**4**) in water by a dotted curve.

In order to learn more about the nature of intermediates the photocyclization of *N*-chloroacetyl-*m*-tyramine (**1**)[6] was studied by flash photolysis. When

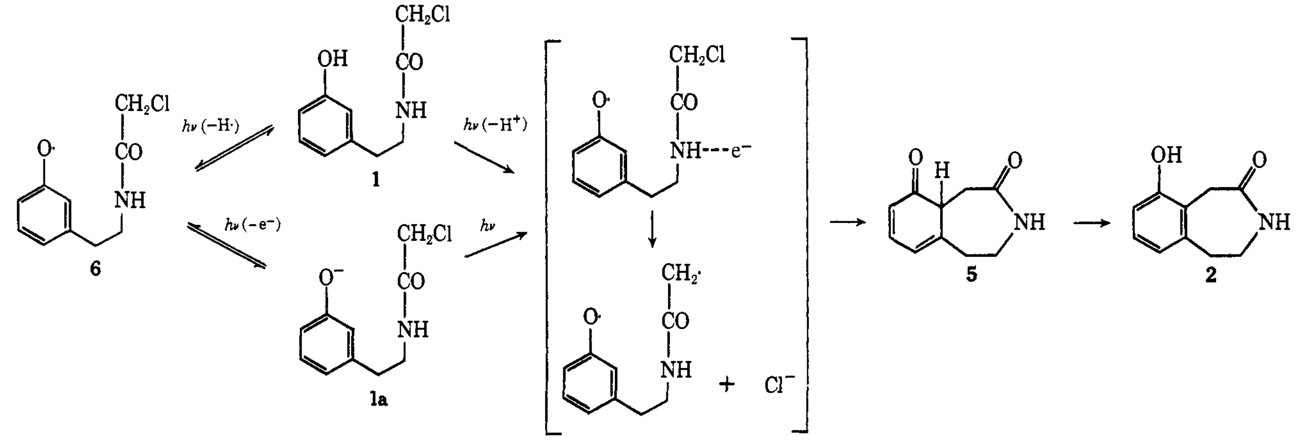


an aqueous solution (2×10^{-4}–$5 \times 10^{-4}M$) of **1** (not degassed) was flash photolyzed[7] at room temperature, a new absorption spectrum of transient species was observed as shown by a solid curve in Figure 1. The spectrum consists of two groups with different intensities and lifetimes.

The weak bands at 380, 386, and 412 nm (τ 200–400 μsec), which were also observed in the flash photolysis of *N*-acetyl-*m*-tyramine (**4**), resemble the absorption bands of the phenoxy radical reported by Grossweiner, *et al.*[4b] (*e.g.*, the phenoxy radical from *m*-cresol: 373, 387, and 412 nm, $\tau > 100$ μsec). Their lifetimes were almost unchanged (−400 μsec) in the alkaline solution (pH 12.4), though the strong bands of the 2,4-dienone decayed somewhat more rapidly under the same condition as described below; therefore, these transient weak bands may be assigned to the corresponding phenoxy radical **6**.

The slower decay of the strong absorption bands at 322 and 330 nm (ε *ca.* 6500, estimated from the absorption intensity) obeys first-order kinetics ($k = 1.9 \times 10^3$ sec^{-1}, τ 530 μsec) and is attributed to another species. This transient species, which was not observed in the photolysis of *N*-acetyl-*m*-tyramine (**4**), must be a fairly long-lived intermediate in the photocyclization of **1**, which we consider to be the ground-state form of the 2,4-dienone **5** for the following reasons. (1) There is no oxygen effect, excluding the possibility of triplet–triplet absorption. (2) Since the phenoxide anion **1a** (**1** at pH 12.4) gave the same spectrum [322 and 330 nm (ε *ca.* 5500), decay $k = 7 \times 10^3$ sec^{-1}, $\tau = 140$ μsec], a radical cationic form of **1** cannot be the transient intermediate. (3) The absorption and emission spectra of *m*-cresol in water were unchanged by the addition of chloroacetamide, an observation which rules out a charge-transfer process. (4) The absorption maxima are almost the same as that predicted by Woodward's rule[8] for 5,5-dialkyl homoannular conjugated cyclohexadienone with an exocyclic double bond (325 nm), and the extinction coefficients are also resonable.[9] Moreover, the more rapid deprotonation of the dienone under alkaline conditions (pH 12.4) would be expected.

Finally this photocyclization was shown to occur by a single-photon mechanism, since the rate of formation of the dienone, determined by absorption changes, was proportional to the light intensity. On the basis of the above evidence, the mechanism of the photocyclization of *N*-chloroacetyl-*m*-tyramine is best described as shown in the scheme.



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(6) In the previous paper, it was reported that a 50% aqueous methanol solution of **1** was irradiated with a 200-W high-pressure mercury lamp to yield mainly **3** (O. Yonemitsu, T. Tokuyama, M. Chaykovsky, and B. Witkop, *J. Amer. Chem. Soc.*, **90**, 776 (1968)). However, the main product from the flash photolysis in water as determined by gas chromatography was **2** (**2**:**3** = 10:1).

(7) The flash photolysis apparatus provided by Nakano Electric Co. was used, the half-width of the photolysis flash light and spectro flash light being about 5 and 3.5 μsec, respectively. The time interval between the two flashes is arbitrarily controlled in the range from 1 μsec to 0.1 sec through a delay circuit. The transient absorption spectra were obtained photographically with Fuji Neopan SS film (ASA 100) by using a Shimazu GE-100 spectrograph.

(8) H. H. Jaffe and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962, p 215.

(9) H. Hart and R. M. Lange, *J. Org. Chem.*, **31**, 3776 (1966); E. C. Friedrich, *ibid.*, **33**, 413 (1968); B. Miller, *ibid.*, **35**, 4262 (1970); B. Miller, *J. Amer. Chem. Soc.*, **92**, 6252 (1970).

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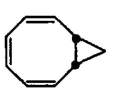
Thermal Isomerization of 1,2,7,8,9,9-Hexadeuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene

Sir:

The detailed mechanism of formation of *cis*-dihydroindene (**2**) from *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) remains unsolved.[1] Neither extensive experimental work in many laboratories over the past decade[2] nor the advent of orbital symmetry theory[3] has led to a completely adequate mechanistic rationale for this facile reaction.



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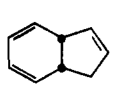

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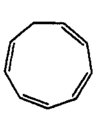

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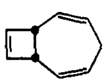
The final step in the overall mechanism is thought to involve the symmetry-allowed conversion of *all-cis*-cyclononatetraene (**3**) to dihydroindene (**2**).[2,4] The penultimate step is imagined to be a nonconcerted biradical-mediated link leading from **1**, or some related structure (**4**–**9**) readily accessible through symmetry-allowed valence isomerizations,[3] to the tetraene **3**.



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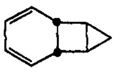

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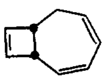

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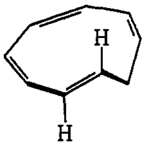

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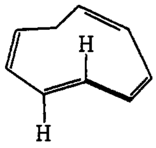

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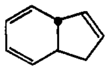

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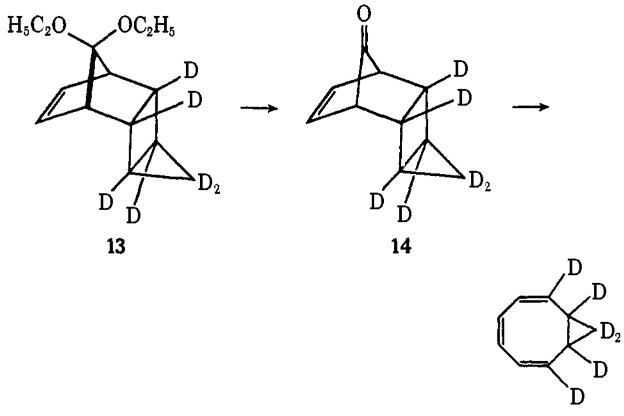
Apparently there has been no consideration of concerted $[_\sigma 2_s + {}_\sigma 2_a]$ processes which might convert **1** or one of the isomers **4**–**9** directly to **2** or **3**; in view of the recently uncovered $[_\sigma 2_s + {}_\sigma 2_a]$ thermal isomerization of 2-methylbicyclo[2.1.0]pent-2-ene (**10**) to 1-methylcyclopentadiene (**11**),[5] analogous reactions seem very reasonable alternatives to the biradical mechanisms commonly invoked as part of the overall **1** → **2** process.

10 **11**

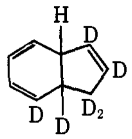
We have prepared and rearranged 1,2,7,8,9,9-hexadeuterio-*cis*-bicyclo[6.1.0]nona-2,4,6-triene (**15**) in an initial test for such $[_\sigma 2_s + {}_\sigma 2_a]$ reactions.



13 **14** **15**

Perdeuteriobicyclo[2.1.0]pent-2-ene[6] and cyclopentadienone diethyl ketal[7] at 4° gave the labeled *endo,anti*-tetracyclo[5.2.1.0^{2,6}.0^{3,5}]dec-8-en-10-one (**13**) in quantitative yield; acid-catalyzed hydrolysis of ketal **13** in aqueous methanol–chloroform gave the corresponding ketone **14**. The nmr spectrum of **13** showed only C-1 and C-7 methine protons at τ 7.25 (t, J = 2.5 Hz) and vinyl protons at 3.89 (t, J = 2.5 Hz) in addition to the two sets of absorptions for $-OCH_2CH_3$; the nmr spectrum of **14** had triplets (J = 2.5 Hz) of equal intensity at τ 3.42 and 7.17, while the carbonyl band in the infrared came at 1780 cm^{-1}.[8]

The glpc-purified labeled ketone **14** in thoroughly degassed neutral CCl_4 was decarbonylated[9] at 120° to provide **15**. Further thermolysis converted **15** to a dihydroindene-d_6 which had nmr absorptions at τ 4.1–4.7 and 6.5 in a ratio of 3.0:1. The complex absorptions found centered at τ 6.98, 7.36, and 7.79 for the other allylic protons in unlabeled dihydroindene (**2**) were completely absent, further supporting the assignment of structure to the 1,1,2,3,7,7a-hexadeuterio compound **16**.



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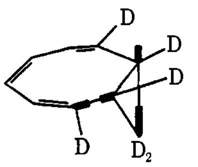

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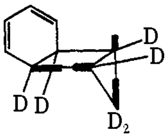

18

This labeling result complements earlier studies limited to tracing the fate of substituents at C-9 in bicyclononatrienes.[2] It conclusively rules out a number of $[_\sigma 2_s + {}_\sigma 2_a]$ mechanisms for the rearrangement, including those abbreviated through structures **17** and **18**. The experimental finding is consistent with the various nonconcerted mechanisms proposed in the literature as well as with the $[_\sigma 2_s + {}_\sigma 2_a]$ symmetry-allowed and connectivity-permuting isomerization of

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(1) J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, **93**, 279 (1971).

(2) Reference 1 includes an extensive listing of pertinent articles.

(3) R. B. Woodward and R. Hoffman, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(4) P. Radlick and W. Fenical, *J. Amer. Chem. Soc.*, **91**, 1560 (1969); P. Radlick and G. Alford, *ibid.*, **91**, 6529 (1969).

(5) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(6) A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, Jr., *Org. Syn.*, submitted for publication; J. E. Baldwin and R. K. Pinschmidt, Jr., *J. Amer. Chem. Soc.*, **92**, 5247 (1970); J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *ibid.*, **92**, 5249 (1970).

(7) E. L. Allred and C. Anderson, *J. Org. Chem.*, **32**, 1874 (1967); P. E. Eaton and R. A. Hudson, *J. Amer. Chem. Soc.*, **87**, 2769 (1965).

(8) The unlabeled analogs of **13** and **14** were thoroughly characterized by mass spectrometric and spectral data; *cf.* J. E. Baldwin and A. H. Andrist, *Spectrosc. Lett.*, in press.

(9) J. E. Baldwin, *Can. J. Chem.*, **44**, 2051 (1966), and references therein.