$\simeq 0$, $D_{cis}{}^{pseudo} = +1.7$, and $D_{trans'}{}^{pseudo} = -3.7$ Hz. The primed interactions are across the cyclobutane ring. We find $C_{3z^2-r^2} = -0.08939$, which corresponds to the ring of carbon atoms tending to be parallel to the applied field direction, as in cyclopropane.

We believe that large methylene rocking motions are the source of our $D_{ij}{}^{pseudo}$ and the relatively large C–H bond lengths we have found.

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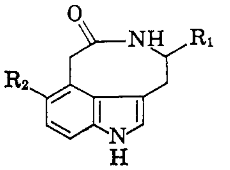
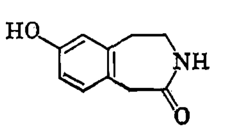
Photolysis of N-Chloroacetyl-O-methyl-L-tyrosine to an Azaazulene

Sir:

The photocyclization of N-chloroacetyl-L-tryptophan provides an easy access to tricyclic indoles of type I.[1] This general and useful preparative method has been applied to other aromatic amino acids and pharmacodynamic amines. For instance, N-chloroacetyl-5-methoxytryptamine gave *dehydromelatonin* (II),[2] and N-chloroacetyl-*m*-tyramine gave 7-hydroxy-1,2,4,5-tetrahydro-3H,3-benzazepin-3-one (III) in 70% yield.[3]



I, R_1 = COOH; R_2 = H
II, R_1 = H; R_2 = OCH_3



III

In all these cases the original chromophore was not changed in the process of photocyclization.

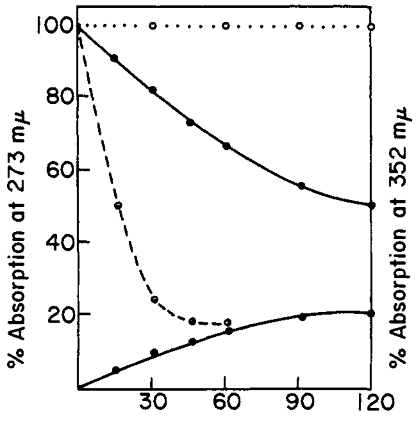


Figure 1. Disappearance of chromophore on irradiation in neutral aqueous solution. Control: N-acetyl-L-tyrosine (–○–○–○); N-chloroacetyl-L-tyrosine (–◒–◒–◒); O-methyl-N-chloroacetyl-L-tyrosine (—●—●—●).

By contrast, the phenolic chromophore of N-chloroacetyl-L-tyrosine on irradiation in aqueous solution (N_2) disappeared rapidly ($t_{1/2}$ = 1.2 min, Figure 1), presumably by formation of secondary products from an unstable intermediate such as a spirocyclohexadienone.[4]

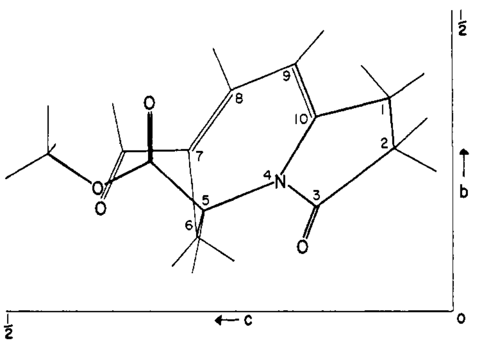


Figure 2. Spatial arrangement of atoms in L-5-carbomethoxy-7-formyl-1,2,5,6-tetrahydro-3H-pyrrolo[1,2-*a*]azepin-3-one (IV).

Irradiation of the homologous O-methyl-N-chloroacetyl-L-tyrosine not only led to slower disappearance of the anisole chromophore but also to the concomitant appearance of a compound with λ_{max} 352 mμ (Figure 1). This compound has now been isolated as a yellow crystalline powder (mp 225° dec) and characterized as its methyl ester, pale yellow needles, mp 145°. Mass spectrometry confirmed the composition of this ester as $C_{12}H_{13}NO_4$.

An X-ray diffraction analysis of a single crystal of $C_{12}H_{13}NO_4$ was made using three-dimensional intensity data which were collected with the equiinclination, multiple-film Weissenberg technique. The material crystallized in the orthorhombic system, space group $P2_12_12_1$, with cell parameters a = 7.17 A, b = 10.08 A, and c = 15.99 A (all ±0.02 A). Phases for the strong and moderately strong reflections were determined directly from the experimental intensities by the symbolic addition procedure[5] for noncentrosymmetric crystals. The atoms in the molecule were located and identified in a three-dimensional density mass computed with the reflections for which phases had been determined. Hydrogen atoms were located on a difference map. The coordinates and anisotropic thermal parameters for each atom were subjected to a least-squares refinement resulting in a final agreement factor of 7.8%. In this way structure IV was deduced with the spatial arrangement indicated in Figure 2.[6] Except for C(6), the carbon and nitrogen atoms in the two rings are nearly coplanar. The ester group is roughly parallel to the aldehyde group.

Nmr and mass spectrometry confirmed this structure (X).[7] The strongest peak (176) next to the parent peak (221 or 235) results from loss of CO_2 or $COOCH_3$. Loss of the aldehyde as CHO (29) gives a significant base peak at 148.

This unusual photolysis of an aromatic ring system is probably initiated by homolysis of the C–Cl bond followed by *ortho* substitution, addition of a Cl (or HO) radical (V → VI), or hydrolysis of the allylic chlorine (see Chart I). Hydrolysis of the vinyl ether might lead to VII, which by retroaldol cleavage would lead to the nine-membered ring VIII. Transannular condensation and (vinylogous) β elimination of the carbinolamide

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(1) O. Yonemitsu, P. Cerutti, and B. Witkop, *J. Am. Chem. Soc.*, **88**, 3941 (1966).

(2) T. Kobayashi and B. Witkop, unpublished results.

(3) M. Chaykovsky, C. M. Foltz, and B. Witkop, unpublished results.

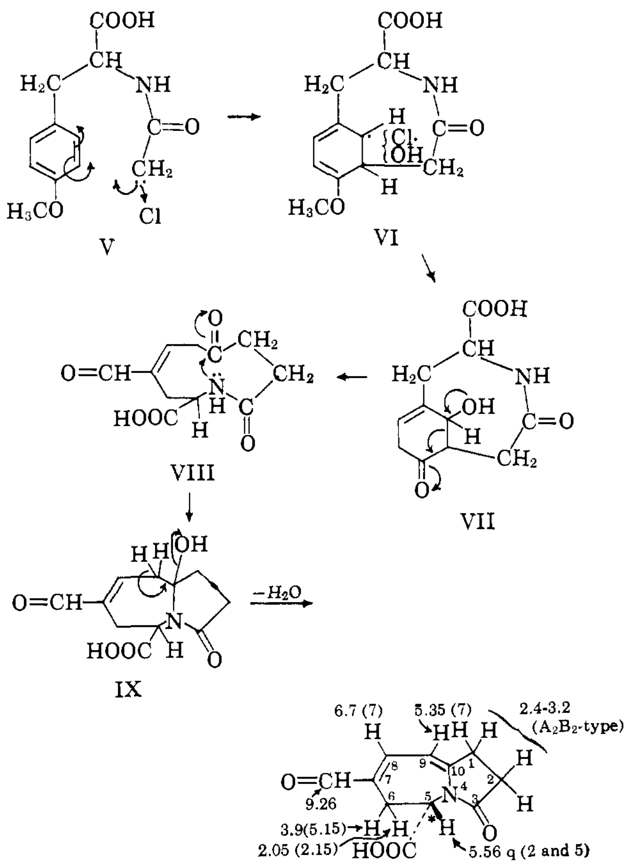
(4) *Cf.* L. Farber and L. A. Cohen, *Biochemistry*, **5**, 1027 (1966). In contrast to these rapid photocyclizations (*under nitrogen*), the slow photooxidation of tyrosine opens up the phenolic ring to aliphatic amino acids: P. G. Gordon, W. A. Jerram, and R. B. Johns, *Biochem. Biophys. Res. Commun.*, **23**, 269 (1966).

(5) I. L. Karle and J. Karle, *Acta Cryst.*, **17**, 835 (1965); J. Karle and I. L. Karle, *ibid.*, **21**, 849 (1966).

(6) I. L. Karle, J. Karle, and J. Estlin, in preparation.

(7) This ring system of a hydrogenated azaazulene was first described by L. A. Cohen and B. Witkop, *J. Am. Chem. Soc.*, **77**, 6595 (1955).

Chart I[a]



IV, R = CH$_3$
X, R = H
(L or *S* configuration)

[a] Values in parentheses are coupling constants, measured in cycles per second.

hydroxyl (IX) would then yield L-5-carboxy-7-formyl-1,2,5,6-tetrahydro-3H-pyrrolo[1,2-*a*]azepin-3-one (X).

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The Unstable Arsinoboron Heterocycle [(CF$_3$)$_2$AsBH$_2$]$_3$[1]

Sir:

The chemical bonding principle first illustrated by the very stable trimer [(CH$_3$)$_2$PBH$_2$]$_3$[2] was extended beyond all expectations by the discovery of [(CF$_3$)$_2$PBH$_2$]$_3$ (stable to 200°),[3] for the existence of which the ring P→B dative bonding alone would not seem to offer an adequate explanation. We now report the discovery of an even less expected analog: the arsenic–boron ring compound [(CF$_3$)$_2$AsBH$_2$]$_3$.

Synthesis. This new trimer was made by mild heating of (CF$_3$)$_2$AsH[4] with B$_2$H$_6$ (stabilized by 1 atm pressure of H$_2$) in a sealed bulb. Most simply, one heats the bottom of the bulb to 40–45° while the top remains at 25° or lower. Within 3–4 days, a trace of a white sublimate will indicate undesirable effects, and the process is stopped. The components are separated completely by high-vacuum fractional condensation, with the desired trimer trapping out at −10° in yields as high as 70% of the consumed reactants. A better way is to heat one side of the bulb to 50–60° by an electric blade, while keeping the bottom at 0°. Convection moves the forming trimer to the 0° region, where it condenses and is stable. One such run (8.5 days) went as follows (millimole stoichiometry).

Table I. Volatility of Liquid [(CF$_3$)$_2$AsBH$_2$]$_3$
(Log $P = 11.0454 + 1.75 \log T - 0.0100T - 3754/T$)
(t_{760} = 178.2°; Trouton constant = 21.2 eu)

Temp, °C	26.4	28.0	30.0	32.2	34.1	35.9
P_{obsd}, mm	0.69	0.80	0.94	1.11	1.32	1.47
P_{calcd}, mm	0.71	0.83	0.94	1.11	1.28	1.47

$$\begin{array}{lllll} 6(CF_3)_2AsH & + \ 3B_2H_6 & \longrightarrow 6H_2 & + \ 2[(CF_3)_2AsBH_2]_3 \\ 0.9731 & 1.892 & \ldots & 0.243 \\ \underline{-0.1178} & \underline{-1.442} & & (85\% \text{ of As}) \\ 0.8553 & 0.450 & & \end{array}$$

A less volatile crystalline by-product probably was [(CF$_3$)$_2$AsBH$_2$]$_4$, for its infrared spectrum (weak at 2490 and 2415 cm^{-1}; strong at 1178, 1148, and 1108 cm^{-1}; medium at 949 and 738 cm^{-1}) was very like that of the trimer when allowance is made for lower frequencies in a Nujol mull.

Characterization. The short melting range (3.0–3.5°) of the trimer and its consistent vapor tensions (Table I) were indicative of purity.

Thermal decomposition to (CF$_3$)$_2$AsH, BF$_3$, and nonvolatile solids made it difficult to work with this trimer above 40°. However, one sample was heated for 1 week at 55–60° with 600 mm pressure of hydrogen, showing only 30% decomposition and apparent inhibition of formation of BF$_3$. Dry HCl failed to affect it while it decomposed slightly during 70 hr at 25°.

The vapor-phase molecular weight was determined by means of a 630-ml immersible tensimeter, in which a sample large enough for accurate weighing all evaporated to register 2 mm pressure, read to 0.01 mm. The average result of four readings (45–51°) was 682 (mean deviation 4.3); calculated, 677.

Proof of Formula. A weighed 0.0969-mmole sample of the trimer reacted with methanol and HCl (98°, 24 hr), forming 0.280 mmole of (CF$_3$)$_2$AsH and 0.546 mmole of H$_2$, respectively 96 and 94% of the calculated values. The excess methanol formed some CH$_3$Cl, from which the (CF$_3$)$_2$AsH could not be completely isolated; hence this arsine was determined by comparing the intensity of its 2142-cm^{-1} infrared peak with that of a known sample at a similar pressure and path length. The slight deficiency of H$_2$ and (CF$_3$)$_2$As groups correlated with a trace of a brown decomposition product.

For boron and confirmation of hydrogen, a 29.8-mg sample (0.132 mmole) was exposed to pure chlorine in excess. Heating to 70° caused a sudden soot formation; then the tube was heated to 400° to make sure of complete reaction. Mercury removed the excess Cl$_2$ and the most volatile fraction was isolated by passage through a high-vacuum trap at −140°. No BCl$_3$ could be found. The product BF$_3$ was isolated

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[1] It is a pleasure to acknowledge the support of this research by the Office of Naval Research, through Contract No. Nonr-228(13), Task Order NR 052 050. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

[3] A. B. Burg and G. Brendel, *ibid.*, **80**, 3198 (1958).

[4] Made by the two methods described by W. R. Cullen, *Can. J. Chem.*, **39**, 1855 (1961).