Table I. The Stoichiometry of the Alanine Oxidation by Air at 25°

Conditions	O_2 reacted,[a] μmoles/ml	Pyruvate formed,[b] μmoles/ml	NH_3 formed,[c] μmoles/ml
Tris buffer, pH 8.1[d]	3.3[e]	3.4[e]	...
Alanine buffer, pH 9.1[f]	3.0[e]	1.3[e]	...
Borate buffer, pH 9.5[g]	4.4[h]	3.3[h]	4.2

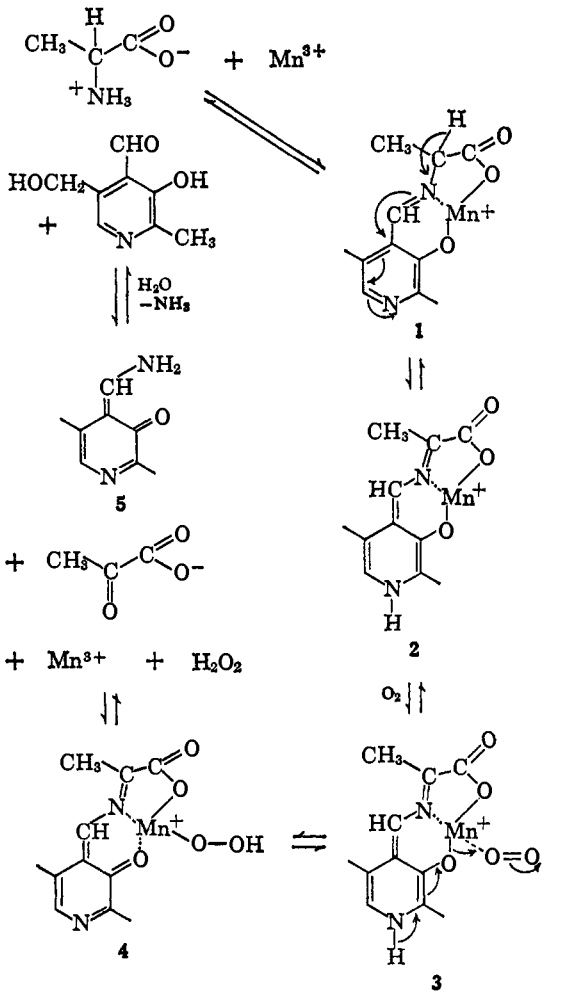
[a] Obtained after subtracting the amount which reacts in the absence of alanine. [b] Determined colorimetrically.[7] [c] Determined by Nesslerization after microdiffusion from the reaction which had gone to completion. [d] Initial concentrations: tris(hydroxymethyl)aminomethane, 0.1 *M*; alanine, 0.04 *M*; Mn^{2+}, 5×10^{-3} *M*; pyridoxal, 5×10^{-3} *M*. [e] Amount reacted or formed during the first hour; with alanine in excess, the O_2 uptake is essentially zero order during this time. [f] Initial concentrations: alanine, 0.08 *M*; Mn^{2+}, 3.3×10^{-5} *M*; pyridoxal, 2×10^{-3} *M*. [g] Initial concentrations: borate, 0.1 *M*; alanine, 5×10^{-3} *M*; Mn^{2+}, 1×10^{-3} *M*; pyridoxal, 5×10^{-3} *M*. A precipitate formed on mixing the reagents. [h] Reacted or formed after 90 min; at this time the uptake of oxygen had stopped; presumably the alanine had all reacted.

is formed[8] but under our conditions appreciable amounts react with other components in the system. At the low concentrations expected in the amino acid oxidation, probably very little O_2 would be formed since its formation requires two molecules of H_2O_2. The low yields of pyruvate can be explained because pyruvate rapidly reacts with H_2O_2. Also, the H_2O_2 may react with the buffer or pyridoxal; we have found that pyridoxal is partially decomposed during the reaction.

Other results which have been obtained with this system include the following: salicylaldehyde and pyridoxine cannot replace pyridoxal but pyridoxal phosphate can; pyridoxamine is apparently not an intermediate because it is oxidized more slowly than alanine, and pyridoxal is a catalyst for pyridoxamine oxidation;[6] α-methylalanine, N-methylalanine, and lactic acid are not oxidized under conditions where alanine reacts readily; other amino acids and amino acid esters and amides can replace alanine but simple amines react slowly if at all with O_2; the rate of O_2 uptake is inhibited by ethylenediaminetetraacetic acid but is unaffected by light or by free radical inhibitors, such as phenols (thus, the oxidation presumably does not occur by a free-radical chain mechanism); glycine is oxidized five to six times more rapidly than α,α-dideuterioglycine.

These results and others are consistent with the mechanism outlined in Chart I. The formation of intermediates **1** and **2** is similar to what has been proposed to explain other pyridoxal-catalyzed reactions of amino acids.[9] It is suggested that **2** or some intermediate like **2** can complex with O_2 to give **3**. The transfer of a proton through the solvent and electrons through the complex, as shown, would lead to **4**, in which the oxygen has been reduced to hydrogen peroxide and the rest of the complex has been oxidized by two electrons. Compound **4** would be expected to be in equilibrium

Chart I



with pyruvic acid, Mn^{3+}, H_2O_2, and **5**. Compound **5** is a tautomer of the Schiff base of ammonia with pyridoxal and would be expected to give pyridoxal and ammonia readily. The H_2O_2 is thought to react in some unspecified way with various components in the system.

It is suggested that the mechanism of the enzymic oxidations of amines is similar to that proposed for the model oxidation. The reasons why manganese ion and amino acids give a conveniently studied model reaction, while copper ion and simple amines are involved in the enzyme reactions, follow from the proposed mechanism and from what is known about other pyridoxal-catalyzed reactions.[9] These will be discussed in subsequent publications.

Gordon A. Hamilton, Agnes Revesz
Frick Chemical Laboratory, Princeton University
Princeton, New Jersey 08540
Received February 5, 1966

(7) *Methods Enzymol.*, 3, 414 (1957).
(8) J. H. Wang, *J. Am. Chem. Soc.*, 77, 4715 (1955).
(9) A. E. Braunstein, *Enzymes*, 2, 113 (1960); E. E. Snell, *Vitamins Hormones*, 16, 77 (1958).

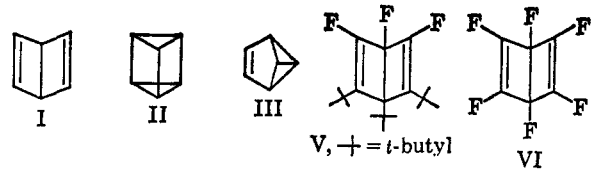
Photoisomerization of Hexafluorobenzene

Sir:

Irradiation of substituted benzenes (which do not have the full D_{6h} symmetry of the parent compound) has been shown[1-6] to give derivatives of Dewar ben-

(1) E. E. Van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, 84, 3789 (1962).
(2) E. E. Van Tamelen and S. P. Pappas, *ibid.*, 85, 3297 (1963).

zene (I), prismane (II), and benzvalene (III). Such valence isomerizations have not been reported in benzene itself, although it has been irradiated at 2537 and 1850 A in the gas phase, in solution, and in solid nitrogen matrix at 4°K.[7] It was of interest to investigate whether a correlation between the rate of photoisomerization of substituted benzenes and their lowered symmetry[8] exists. Results on the irradiation of hexafluorobenzene IV are reported here.



Irradiation of hexafluorobenzene vapor at 35 mm at 25° with an unfiltered medium-pressure mercury arc gave a single volatile product (mp 6.0°). The initial quantum yield for its formation was of the order of 0.003 but the conversion was limited to about 10% by the simultaneous deposition of a yellow polymer on the windows of the cell. Gas chromatography on temperature-programmed (25° until 20 min, 2.9°/min thereafter), 10-ft diisodecyl phthalate column served to separate the product from unreacted hexafluorobenzene. Retention times were 6.1 and 36.5 min, respectively. The product thus isolated gave only a single, sharp peak on a KEL-F Oil No. 3 column. No decomposition was observed on either of these columns. The structure of the product was deduced from the following evidence. The molecular weight (mass spectrum) of 186 and the analysis (C, 39.04; F, 60.40; C_6F_6 requires C, 38.73; F, 61.27) showed that the product was isomeric to IV. In its ultraviolet spectrum (vapor) the compound showed end absorption (ϵ_{2200} 950; ϵ_{2100} 1800) but no maximum above 2000 A. This excluded a conjugated diene structure such as fulvene. The fluorine nmr spectrum[9] showed only two signals with an intensity ratio 2:1 at 121.2 and 190.1 ppm. The chemical shifts of the fluorine atoms in V have been reported[10] to lie at +103 and +181 ppm, the bridgehead fluorine being at the higher value. These data suggest that the photoisomer of hexafluorobenzene is hexafluorobicyclo[2.2.0]hexa-2,5-diene (VI). The F–F coupling constants are less than 3 cps, which is of the same order as the reported values[10] in V. The infrared spectrum (vapor) of VI showed bands at 1751 (s), 1339 (vs), 1269 (w), 1235 (m), 1074 (vs), 924 (vs), 886 (vs), 817 (w), and 671 (w) cm^{-1}; the first of these confirms the presence of fluorine-substituted –C=C– bonds,[11] and the number of allowed fundamentals is in agreement with a structure of reasonably low symmetry. VI is stable as a solid at −20° and in CCl_4 solution at room temperature. Irradiation at 1850 A converted it into IV and some solid polymer.

The irradiation of hexafluorobenzene (i) in methylcyclohexane solution at 2537 A, (ii) in ether solution at 2850–3200 A, (iii) in cyclohexane solution at >3025 A in the presence of benzophenone as sensitizer, or (iv) in the gas phase at 2537 A with mercury as sensitizer resulted in a mixture of as yet unidentified but mostly higher molecular weight products. Under these conditions VI was notably absent from the product mixture as shown by gas chromatography under the same conditions as used in the direct vapor-phase photolysis. Since the products formed in (iii) and (iv) must arise from triplet hexafluorobenzene, these results indicate that in the photoisomerization of hexafluorobenzene to VI the triplet is not the excited state involved.

The formation of hexafluoro(Dewar benzene) from IV indicates that steric effects or the reduction of the benzene symmetry by substituents is not a precondition for valence isomerization. The stabilization of small rings by fluorine substituents is well known.[12]

Kaplan, *et al.*,[5] recently reported that in the photoisomerization of xylenes in the gas phase only 1,2 migration of the methyl groups takes place, while in solution both 1,2 and 1,3 shifts occur. This led them to conclude that it is sufficient to postulate that the intermediate in the gas phase is of a benzvalene structure, whereas in solution either a prismane, or a set of easily interconvertible Dewar structures, or both, may serve as intermediates. If the present results on hexafluorobenzene can be extrapolated to a disubstituted benzene, such as xylene, then it is possible to narrow down the alternatives in the solution photolysis of the xylenes. The isolation of a Dewar benzene in the gas-phase photolysis of IV is compatible with the absence of 1,3 shifts in the xylene system only if the condition of easy interconvertibility of Dewar structures, required for the interchange of the ring carbons, is not met. This, in turn, indicates that the prismane structure is the intermediate in the 1,3 migrations in solution.

Acknowledgment. Valuable discussions with Dr. R. Srinivasan are gratefully acknowledged.

(3) A. W. Burgstahler, P. L. Chien, and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **86**, 5281 (1964).

(4) E. M. Arnett and J. M. Bollinger, *Tetrahedron Letters*, 3803 (1964).

(5) L. Kaplan, K. E. Wilzbach, W. G. Brown, and S. S. Yang, *J. Am. Chem. Soc.*, **87**, 676 (1965).

(6) K. E. Wilzbach and L. Kaplan, *ibid.*, 87, 4004 (1965).

(7) I. Haller and R. Srinivasan, unpublished results. The limits of detection corresponded to a quantum yield of 10^{-4}.

(8) It is felt that, since Dewar benzene is known[2] to have a reasonable stability, the valence isomers are not formed at all in the irradiation of benzene.

(9) The nmr spectra were recorded by Dr. E. R. Malinovski of Stevens Institute of Technology. Chemical shifts are referred to CCl_3F internal standard; calibrations were effected by the sideband technique.

(10) H. G. Viehe, R. Merenyi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem. Intern. Ed. Engl.*, **3**, 755 (1964).

(11) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 42.

(12) A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958.

Ivan Haller
IBM Watson Research Center
Yorktown Heights, New York
Received February 25, 1966

Photochemical Reactions of Camphorquinone[1]

Sir:

Whereas the photochemistry of monoketones has received a great deal of attention, the photochemistry of α-diketones has been explored to a much smaller extent. One of the most interesting discoveries in this area was that of Urry, *et al.*, who found that simple aliphatic α-diketones (such as 5,6-decanedione (I)) undergo facile photocyclization in benzene solution to form 2-hydroxy-

(1) The partial support of this research by the National Science Foundation (Grant No. GP-4128) is acknowledged with pleasure.