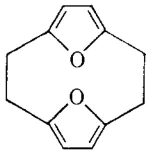
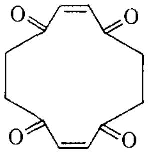
this reaction could lead to the macrocyclic unsaturated tetraketone II, if, as observed in the related reaction with bromine and methanol,[3-5] both furan rings undergo oxidation.

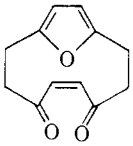


I

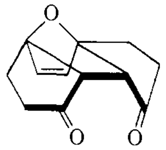


II

We wish to report that on exposure of I to air in an ethanolic solution containing methylene blue, during irradiation with a 150-watt floodlamp, partial oxidation takes place yielding the bicyclic diketone IV (or *exo* isomer) as the main product. The reaction appears to take place through intermediate III, which incorporates diene and dienophile in a particularly favorable geometry for an intramolecular Diels-Alder reaction.[6]



III

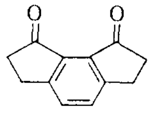


IV

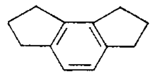
The proof of structure of IV which is outlined below does not discriminate between the *endo* form, shown above, or the *exo* form.

The photoöxidation product IV, formed in 42% yield, m.p. 186–187° (dec.), shows a single carbonyl peak in the infrared at 1740 cm.$^{-1}$ ($CHCl_3$) and no aromatic (furanoid) absorption in the ultraviolet. (*Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92; mol. wt., 204. Found: C, 70.73; H, 6.14; mol. wt., 204, 216). Hydrogenation of the double bond in IV with palladium on charcoal in ethanol gave the dihydro derivative V, m.p. 150.5–151°. (*Anal.* Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.91; H, 6.96). The n.m.r. spectrum of V, exhibiting, among other peaks, a singlet at 7.26 τ corresponding to the two tertiary protons α- to the carbonyl group, and a singlet at 8.08 τ (four protons at the site of the hydrogenated double bond) is completely consistent with the proposed structure.

Treatment of IV with dilute sulfuric acid yielded 1,8-dioxo-2,3,6,7-tetrahydro-*as*-indacene (VI) m.p. 208–209.5° (dec.). (*Anal.* Calcd. for $C_{12}H_{10}O_2$: C, 77.40; H, 5.41. Found: C, 77.32; H, 5.47; $\lambda_{\max}^{95\%\,\mathrm{EtOH}}$: 257 m$\mu$ (ϵ 7750), 264 mμ (ϵ 6950), 313 mμ (ϵ 4560), 321 mμ (ϵ 4220); $\lambda_{\max}^{\mathrm{CHCl_3}}$ 3010, 1715, 1601, 832 cm.$^{-1}$. The n.m.r. spectrum shows a singlet at 2.34 τ corresponding to the two aromatic hydrogens and a typical A_2B_2 spectrum centered at 7.05 τ, corresponding to the eight remaining protons.



VI



VII

The carbon skeleton in IV, V and VI was conclusively established by hydrogenation of IV (palladium on charcoal) to the known hydrocarbon, 1,2,3,6,7,8-hexahydro-*as*-indacene (VII). The hydrogenation product (VII) m.p. 38–40° is identical (superimposable infrared and ultraviolet absorption spectra, mixture melting point) with an authentic sample prepared through an independent route by Rapoport and Smolinsky.[7]

Further studies on the stereochemistry of IV, and on furan photoöxidations are in progress.

bald, *J. Am. Chem. Soc.*, **82**, 1428 (1960). In this work, compound I was prepared by the procedure outlined by Winberg and co-workers. The initial studies were carried out on a sample kindly provided by Dr. Winberg.

(4) D. J. Cram and G. R. Knox, *ibid.*, **83**, 2204 (1961).

(5) N. Clauson-Kaas, *Kgl. Danske Videnskab. Selskab. Mat-fys. Medd.*, **23** (6), 18 (1947).

(6) A related intramolecular process may be involved in the reaction of I with dicarbomethoxyacetylene, ref. 4.

(7) H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.*, **82**, 1171 1960). We wish to thank Prof. Rapoport for providing us with a sample of 1,2,3,6,7,8-hexahydro-*as*-indacene for comparison.

CONTRIBUTION NO. 1719 FROM HARRY H. WASSERMAN
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RECEIVED OCTOBER 17, 1962

PHOTOCHEMICAL PREPARATION OF XENON DIFLUORIDE[1]

Sir:

When Claassen, Selig and Malm of this laboratory first reported XeF_4, they also suggested the existence of a lower fluoride of xenon.[2] Further evidence for this lower fluoride was found by Studier and Sloth,[3] who, in mass spectrometric studies, have observed XeF_2 as a minor component of the xenon fluorides prepared by thermal reaction of xenon and fluorine. We have now prepared XeF_2 in relatively pure form by the photochemically induced reaction of xenon and fluorine at room temperature. The light source was a 1000-watt General Electric AH-6 high pressure mercury arc. Both the arc and the water-cooled jacket were of fused silica. Fused silica lenses concentrated the light in a narrow intense beam. The ultraviolet absorption spectrum of gaseous fluorine[4] is a continuum with a maximum at 2900 Å. The effective wave lengths in our work are probably about 2500–3500 Å. and presumably produce F atoms.

Early preparations were carried out by irradiating in fused silica vessels, but SiF_4 produced by attack on the cell by fluorine made analyses difficult. All of the work reported herein, except for one run, made use of an all-nickel system with synthetic sapphire windows. The cell was of a closed-loop design consisting of a reservoir of about 400 cc., the sapphire windowed reaction chamber of nearly 100 cc., and 8 mm i.d. nickel tubing completing a loop. Circulation was effected by use of a heating tape operated at near 90° on one leg of the loop. The

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) H. H. Claassen, H. Selig and J. G. Malm, *J. Am. Chem. Soc.*, **84**, 3593 (1962).

(3) M. H. Studier and E. N. Sloth, *J. Phys. Chem.*, in press; *Science*, **138**, 136 (1962).

(4) H. V. Wartenberg, G. Sprenger and J. Taylor, *Z. physik. Chem.*, Bodenstein-Festband, Akademische Verlagsgesellschaft m.b.H. Leipzig, 1931, p. 61.

bottom "U-bend" was kept in a −80° bath during the irradiations in order to freeze down the product. A water-cooling coil kept the nickel walls of the light absorbing chamber at about room temperature. A metal pressure gage of the Bourdon type was used to observe the reaction rate during irradiation.

The photochemical data are summarized in Table I. The product ratio, F_2/Xe (last column), was calculated from results of chemical analyses made by heating the product with an excess of H_2 for one hour at 400°, and subsequent separate weighings of xenon and hydrogen fluoride trapped and transferred to weighing cans.[2] The relative proportions of F_2 and Xe reacting also were confirmed by pressure measurements made with and without the use of liquid O_2 to freeze down the xenon. A F_2/Xe ratio of 0.89 found for run 1 may be in error due to impurities introduced by the use of a silica vessel. With this exception, the ratios correspond to the formation of relatively pure XeF_2. A Bendix time-of-flight mass spectrometer showed principally XeF_2 and traces of XeF_4 in our samples. No oxyfluorides were observed. Studies on the infrared spectra of the products of some of the irradiations showed an intense band with peaks at 549 and 565 cm.$^{-1}$ due to XeF_2 and showed no absorption at 590 cm.$^{-1}$ where the XeF_4 has a strong absorption.[2] It is estimated that 1% of XeF_4 would have been detected by this method.

TABLE I
PHOTOLYSIS OF Xe AND F_2

Run	Initial pressure Mm. F_2 + Xe	Initial pressure Ratio F_2/Xe	Final press., mm. F_2 + Xe	Product coll., g.	Anal. prod. ratio, F_2/Xe
1[a]	990	2.00	447	0.31	0.89
2	890	2.35	546	0.73	1.04
3	979	5.20	640	0.61	0.98
4	1030	0.91	73	2.11	1.01
5	971	5.03	654	0.60	1.01

[a] Run in silica vessel; all other runs in nickel system with sapphire windows.

XeF_2, much like XeF_4, is a solid at room temperature and easily forms crystals which can be made to sublime readily or to grow on a slightly cooled wall of a containing vessel. X-Ray diffraction patterns of samples produced in either quartz or nickel cells are identical. Room temperature powder patterns of samples which have been condensed at liquid nitrogen temperatures from the vapor indicate that the cell is body-centered tetragonal with a = 4.316 kx. and c = 6.993 kx. Single crystals grown from the vapor phase at room temperature also give the same symmetry and cell dimensions. No vapor pressure measurements have been attempted, but XeF_2 appears to have a room temperature vapor pressure of about 2 mm.

A quantum yield for Xe reacted has been determined. For this work, an Osram HBO 500 mercury arc was used with a fused silica lens to give a fairly uniform, parallel beam. A chemical filter solution[5] was used in a 4 cm. length fused silica cell placed just behind the lens. This solution transmitted about 70% of the 2500–3200 Å. light from the lamp and less than 1% of wave lengths outside the 2200–3400 region. Uranyl oxalate actinometry was used with the sapphire-windowed cell. The initial F_2/Xe ratio in the cell was 0.95. During the irradiation the total pressure decreased from 966 to 791 mm. Using a quantum yield for the actinometer of 0.60 as effective in this spectral range, the preliminary value of the quantum yield for Xe reacted was found to be 0.3,[6] showing a rather efficient photochemical reaction. Typically, the rate of pressure decrease falls as reactants are used up. It is not yet known how the quantum yield may vary with pressure or intensity.

Negative results were obtained when several other reactions were tried under conditions similar to the xenon plus fluorine photolyses. These were: Kr and F_2 (this mixture also was irradiated at −60° with negative results), Xe and Cl_2, Rn and Cl_2, and Xe and O_2. This last mixture was irradiated with 1849 Å. light from a low pressure mercury resonance lamp.

Further experiments designed to give information on the mechanism of the photolysis of xenon and fluorine are planned.

We wish to thank several Argonne staff members for their cooperation: M. Studier and E. Sloth for the mass spectrometry, H. Claassen for the infrared, and S. Siegel for the crystallographic studies.

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(5) M. Kasha, *J. Opt. Soc. Am.*, **38**, 929 (1948).

(6) Correction for dark reaction due to heating tape. Quantum yield of 0.3 also found without heating tape, when no dark correction is needed.

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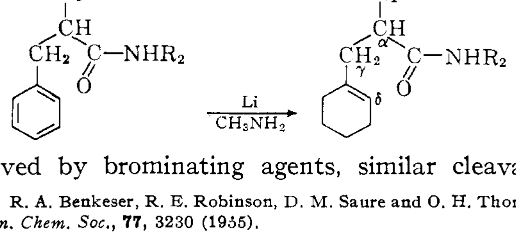
RECEIVED NOVEMBER 5, 1962

NON-ENZYMATIC CLEAVAGE OF PHENYLALANYL PEPTIDE BONDS

Sir:

We wish to report a chemical cleavage of phenylalanyl peptide bonds utilizing "Birch reduction"[1] of the aromatic ring and an oxidative cleavage with N-bromosuccinimide.[2–5]

Partial reduction of ethylbenzene (1) by the Birch reduction leads to 1-ethylcyclohexene. It might be expected that such a reduction of phenylalanyl peptides would lead to a double bond γ–δ with respect to the carbonyl of the peptide. Since tryptophyl (2), tyrosyl (4) and histidyl (5) peptides which all contain γ–δ double bonds are



cleaved by brominating agents, similar cleavage

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(1) R. A. Benkeser, R. E. Robinson, D. M. Saure and O. H. Thomas, *J. Am. Chem. Soc.*, **77**, 3230 (1955).

(2) A. Patchornik, W. B. Lawson, E. Gross and B. Witkop, *ibid.*, **82**, 5923 (1960).

(3) N. Izumiya, J. E. Francis, A. V. Robertson and B. Witkop, *ibid.*, **84**, 1702 (1962).

(4) G. L. Schmir, L. A. Cohen and B. W. Witkop, *ibid.*, **81**, 2228 (1959).

(5) Sh. Shaltiel and A. Patchornik, *Bull. Res. Coun. Israel*, **10A**, 79 (1961).