Table I. Reactions of **1c** with Lead Tetraacetate[a]

Solvent	Additives	Time, hr	Yield,[b] moles/mole of **1c** *p*-MeO-$(Ph)_2CO$	$(Ph)_2CO$	Mig apt[c] *p*-MeO-Ph–:Ph–
PhH	...	95	0.218	0.370	3.4
PhH[d]	Py[e]	23	0.248	0.206	1.7
PhH	Cu[f]	22	0.343	0.203	1.2
PhH[d]	Py,[e] Cu[f]	1.5	0.162	0.0855	1.1
PhH	$PhNO_2$[g]	100	0.0934	0.570	12
MeCN	...	95	0.0883	0.578	13
MeCN	Py[h]	19	0.122	0.202	3.3
MeCN	Cu[i]	22	0.205	0.365	3.6
MeCN	Py,[h] Cu[i]	18	0.153	0.0977	1.3
MeCN	$PhNO_2$[j]	95	0.0590	0.464	16

[a] **1c**, 3.27 mmoles; $Pb(OAc)_4$, 7.22 mmoles unless noted otherwise; solvent, 20 ml unless noted otherwise; $CaCO_3$, 15.0 mmoles (used only in experiments without pyridine); 82 ± 2°. Oxygen had no effect on results. [b] Analyses by glpc; yields of ketals included. [c] 2 [moles of $(Ph)_2CO$]/moles of *p*-$MeO(Ph)_2CO$. [d] 25 ml; $Pb(OAc)_4$, 9.83 mmoles. [e] Pyridine, 19.7 mmoles. [f] Harshaw "Uversol copper liquid 8%," equivalent to 1.00 g-atom of Cu. [g] 3.27 mmoles. [h] Pyridine, 14.5 mmoles. [i] $Cu(OAc)_2 \cdot H_2O$, 1.00 mmole. [j] 6.54 mmoles.

However, the alkoxy radical mechanism is not the only one through which the rearrangement can proceed. In the case of **1c**, the occurrence of *two* mechanisms is clearly shown by the marked influence of reaction conditions upon the *p*-methoxyphenyl:phenyl migratory ratio (Table I). The low ratios obtained with pyridine and copper salts are believed to reflect the predominant operation of the alkoxy radical mechanism,[8,11] while the high values obtained in acetonitrile and the experiments using nitrobenzene are consistent with the preferential decomposition of a first-formed Pb(IV) alcoholate *via* a concerted, quasiionic[11] process (either heterolytic or homolytic) involving aryl participation. Our results suggest that the quasiionic mechanism is likely to be observed only in cases where neighboring groups bearing strongly electron-donating substituents are near the hydroxyl function.

Since nitrobenzene caused no marked increases in reaction rate or hemiketal ester yields, did not cause the formation of new products, failed to reduce the over-all material balance (based on **1c**), and was not used in large enough concentration to affect medium polarity significantly, its effect upon the *p*-methoxyphenyl:phenyl ratio is apparently due to selective inhibition[6a] of a radical *chain* process rather than to selective acceleration of the quasiionic mode. A scheme which accounts for the available facts relating to the radical mechanism is shown below.[12]

Initiation

$$Ar_3COH + Pb(OAc)_4 \longrightarrow Ar_3COPb(OAc)_3 + HOAc$$

$$Ar_3COPb(OAc)_3 \longrightarrow Ar_3CO\cdot + (AcO)_3Pb\cdot$$

Propagation

$$Ar_3CO\cdot \longrightarrow Ar_2COAr$$

$$Ar_2COAr + Ar_3COPb(OAc)_3 \longrightarrow \mathbf{2} + Ar_3COPb(OAc)_2$$

$$Ar_3COPb(OAc)_2 \longrightarrow Pb(OAc)_2 + Ar_3CO\cdot$$

Termination

$$Ar_2COAr + (AcO)_3Pb\cdot \longrightarrow \mathbf{2} + Pb(OAc)_2$$

In view of the foregoing observations, the occurrence of radical chain mechanisms in the oxidation of other types of monohydric alcohols with lead tetraacetate seems highly probable.

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W. H. Starnes, Jr.
Esso Research and Engineering Company
Baytown Research and Development Division
Baytown, Texas 77520
Received April 7, 1967

New Syntheses of Alloxazines[1]

Sir:

Alloxazines and isoalloxazines[2] are customarily prepared by condensation of (a) an *o*-phenylenediamine with alloxan,[3] (b) a 4,5-diaminopyrimidine with an *o*-benzoquinone,[4] (c) an *o*-aminoazobenzene with a barbituric acid,[5] (d) a 5-nitrosopyrimidine with an aromatic amine[6] or an *o*-phenylenediamine,[7] or (e) by nitrosation of a 6-arylaminouracil.[8] We wish to report three new synthetic approaches to alloxazines which not only are applicable, in principle, to the preparation of other condensed pyrazine heterocycles, but which offer further versatility in the synthesis of alloxazines with different origins for N_5 and N_{10}.

Method A. Recent studies on the deoxygenation of aromatic nitro compounds by triethyl phosphite[9] support the intermediacy of nitrene intermediates. Capture of these nitrenes by intramolecular insertion has been utilized for the preparation of a number of heterocyclic systems (carbazoles,[10] benzotriazoles,[10] indazoles,[10] phenothiazines,[11] anthranils,[11] indoles,[10,12] pyrrolo[3,2-*d*]pyrimidines[13]). We report the first application of this procedure to the synthesis of a condensed pyrazine system. Thus, refluxing 1,3-di-

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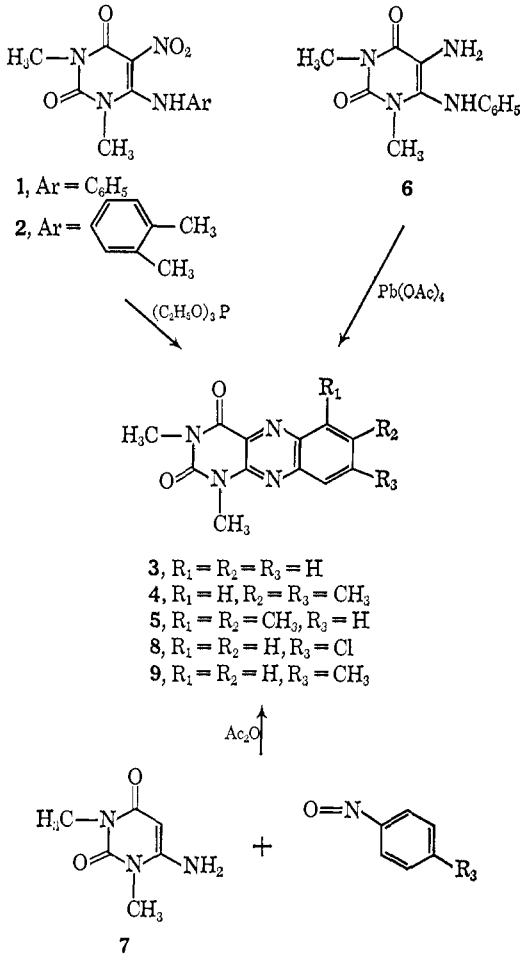
(11) *p*-Methoxyphenyl:phenyl migratory ratios for alkoxy radical rearrangements have apparently not been reported previously. However, the groups are known to show comparable reactivities in the homolytic neophyl rearrangement [C. Rüchardt and R. Hecht, *Tetrahedron Letters*, 961 (1962)]. Ionic decompositions of *p*-methoxytriphenylmethyl hydroperoxide[7b] and the corresponding perbenzoate (I. J. Levine, Ph.D. Thesis, University of Kansas, 1960) give preferential *p*-methoxyphenyl migration.

(12) A similar scheme which does not involve Pb(III) species is also possible.

methyl-5-nitro-6-anilinouracil (**1**), mp 200.1°, in excess triethyl phosphite under N_2 for **2** hr, removal of volatiles by partial evaporation under a vigorous stream of N_2, and dilution with ethanol gave 1,3-dimethylalloxazine (**3**),[14] mp 243.3°[8] (30%). It is of considerable interest that the major product of this reaction was 1,3-dimethyl-6-anilinouracil, mp 187.7°.[8] To our knowledge, this is the first example of *de*nitration in the pyrimidine series. Similarly, heating 1,3-dimethyl-5-nitro-6-(3,4-xylidino)uracil (**2**), mp 212–214°, in triethyl phosphite for 7.5 hr gave a mixture of 1,3,7,8-tetramethylalloxazine (**4**), mp 253–254°[15] (14%), and 1,3,6,7-tetramethylalloxazine (**5**), mp 273.3°, along with the product of denitration, 1,3-dimethyl-6-(3,4-xylidino)uracil, mp 233.6°.

Method B. 1,3-Dimethylalloxazine (**3**) was prepared in 61% yield by portionwise addition of 1.5 moles of lead tetraacetate to a refluxing ether suspension of 1,3-dimethyl-5-amino-6-anilinouracil (**6**), mp 160.3°, followed by filtration and washing with water. The same conversion could be effected in lower yield (48%) by heating an intimate mixture of **6** with lead dioxide at 220°.



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Method C. Refluxing 1 equiv of 1,3-dimethyl-6-aminouracil (**7**) with 2 equiv of nitrosobenzene, *p*-chloronitrosobenzene, or *p*-nitrosotoluene in acetic anhydride for 15 min, followed by dilution with water, gave 1,3-dimethylalloxazine (**3**), 52%, 1,3-dimethyl-8-chloroalloxazine (**8**), mp 251.0° (68%), and 1,3,8-trimethylalloxazine (**9**) mp 251.7° (49%). This latter compound was identical with the product of previously undetermined structure (1,3,6- or 1,3,8-trimethylalloxazine, mp 252–253°) prepared by nitrosation of 1,3-dimethyl-6-(*p*-toluidino)uracil.[8]

Applications of these procedures to the preparation of other condensed pyrazine heterocycles are in progress.

(14) Satisfactory microanalytical and spectral data were obtained for all compounds reported.

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Edward C. Taylor, Frank Sowinski, Tucker Yee, Fumio Yoneda
Department of Chemistry, Princeton University
Princeton, New Jersey
Received May 3, 1967

Correlation between the Photochemistry and the Mass Spectra of Pyruvic Acid and Isopropyl Pyruvate[1,2]

Sir:

We wish to report an interesting correlation between the mass spectral behavior and photochemistry of both pyruvic acid and its isopropyl ester. Although processes which are general in photolyses have long been known to have analogs in mass spectral fragmentations,[1] *the cases reported here are examples of unusual behavior of two molecular ions which are paralleled by unusual behavior of two corresponding n,π* excited states.* Such an observation is significant in that it provides evidence for the validity of attempts to interrelate the mass spectrometry and photochemistry of organic molecules.

Photolysis of pyruvic acid in the vapor phase[3] and in aqueous solution[4] yields acetaldehyde and CO_2, and acetoin, respectively. The reaction has been proposed to involve an n,π* state which forms an uncommon five-membered transition state.[5] The latter collapses to CO_2 and methylhydroxycarbene which then rearranges to acetaldehyde. From Table I it can be seen that the analogous process occurs in the mass

Table I. Partial Monoisotopic Mass Spectra (75 ev) of Pyruvic Acid and Pyruvic Acid-OD[a]

CH_3COCO_2H		CH_3COCO_2D[b]	
%	Ion	%	Ion
4.2	$C_3H_4O_3$	4.2	$C_3H_3DO_3$
16	CHO_2	22	CDO_2
3.4	C_2H_4O	6.7	C_2H_3DO
100	C_2H_3O	5.8	C_2H_2DO
		100	C_2H_3O

[a] Empirical formulas were determined by exact mass measurement on a CEC 21-110B mass spectrometer. Inlet system and source were maintained below 70° to avoid thermal decomposition. [b] Prepared by injecting a solution of pyruvic acid in a ten-volume (~40 mole) excess of D_2O into the spectrometer previously equilibrated with D_2O. Relative abundances corrected to 100% d_1.

(1) Part II in this series; see N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D'Angelo, *J. Am. Chem. Soc.*, 87, 4079 (1964) for part I.

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