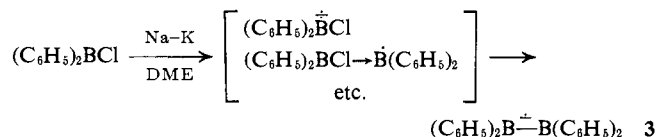


3 on the basis of hyperfine structure ($a_{B_1} = a_{B_2} = 2.1$ gauss, $a_H = 0.58$ gauss) is observed after the decay of a more complex spectrum. The spectrum assigned to 3 is succeeded in turn by one whose hyperfine structure still suggests strong interaction with two boron nuclei, but also strong interaction with a single hydrogen atom and weak interaction with only eight hydrogens. This large decrease in the number of weakly interacting hydrogens probably means that the decomposition of 3 is accompanied by the loss of two phenyl groups. A still later and final e.s.r. signal observed after further reaction with the alkali metal is the highly characteristic hyperfine spectrum of the biphenyl anion radical.^{3,4} Similar e.s.r. series terminating in the spectrum of the biphenyl anion radical are observed in experiments starting with triphenylboron or diphenylborinic anhydride in place of the diphenylboron chloride.



The cleavage of aryl groups from aryl boron is supported not only by the formation of 1 from trimesitylboron but also by the isolation of phenylboronic anhydride in some of our trapping experiments with mixtures of radicals from diphenylboron chloride. In a univalent intermediate such as phenylboron the two nonbonding electrons can occupy a low energy 2s orbital.

Acknowledgment. We are pleased to acknowledge the support of this work by the Army Research Office (Durham) and by the Atomic Energy Commission.

(3) A. Carrington and J. dos Santos-Veiga, *Mol. Phys.*, **5**, 21 (1962).

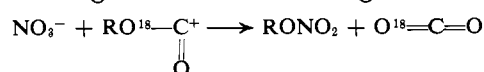
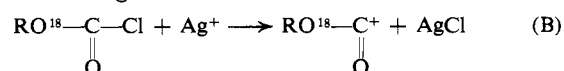
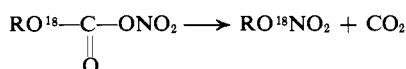
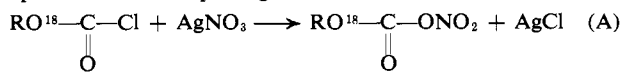
(4) It is interesting to note that the oxidation of tetraphenylborate ion also gives biphenyl, apparently by an intramolecular mechanism: D. H. Geske, *J. Phys. Chem.*, **66**, 1743 (1962).

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Reaction of Methyl Chloroformate with Silver Nitrate. A New Approach to Evidence for an Intermediate Anion in Replacement Reactions at Carbonyl Carbon

Sir:

The reaction of chloroformate esters with an acetonitrile solution of silver nitrate has been proposed as an excellent method for the synthesis of nitrate esters.^{1,2} To explain the 75% retention of the alkyl oxygen bond during a reaction of *n*-hexyl chloroformate, Boschan¹ proposed two competing mechanisms



(1) R. Boschan, *J. Am. Chem. Soc.*, **81**, 3341 (1959).

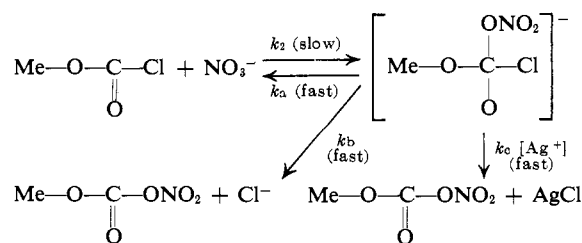
(2) G. A. Mortimer, *J. Org. Chem.*, **27**, 1876 (1962).

Under conditions for which silver nitrate reacts readily with an acetonitrile solution of methyl chloroformate, silver perchlorate showed no reaction even after 6 days. Similarly, as described below, addition of silver perchlorate to a solution of silver nitrate reacting with methyl chloroformate produced a slight retardation in rate. It is clear that direct electrophilic assistance to chloride ion removal, as proposed in reaction B, does not operate.

Reaction of methyl chloroformate with silver nitrate at 25.0°, as followed by titration of soluble silver ion, gave good second-order kinetics during at least the first 25% of reaction. The values for the second-order rate coefficient, k_2° , fell with increasing initial concentration of silver nitrate. Both the kinetics and the positions of bond fission can be rationalized by assuming that reaction always proceeds through an intermediate nitrateformate ester which then decomposes to nitrate ester by two competing mechanisms.

Boschan,¹ in proposing mechanism A, assumed that the nitrateformate ester decomposes through a four-centered transition state. However, it is attractive to consider the possibility of the nitrateformate ester decomposing through two competing ionic mechanisms. These two mechanisms can be considered to involve ionization to give ion pairs containing either nitronium ions or nitrate ions; these can then lead to nitrate ester by attack on the appropriate counterion. Such an ionization scheme would be consistent with one previously proposed by Burton and Praill³ for acyl nitrates. This aspect of the over-all scheme is currently under investigation.

The reaction scheme proposed for the formation of methyl nitrateformate can be expressed as



It follows that the observed second-order rate coefficient, k_2° , will be related to the silver nitrate concentration by the expression

$$k_2^\circ = \frac{k_2 k_b \alpha / (k_a + k_b) + [k_2 k_c \alpha^2 / (k_a + k_b)] [AgNO_3]}{1 + [k_c \alpha / (k_a + k_b)] [AgNO_3]}$$

The values for α , the degree of dissociation of silver nitrate at concentration $[AgNO_3]$, can be calculated using a value⁴ for the dissociation constant of silver nitrate of 0.015 mole/l.

The mean value of 2.00×10^{-4} l. mole⁻¹ sec.⁻¹ for the second-order rate coefficient for reaction of methyl chloroformate with 0.005 *M* to 0.04 *M* concentrations of tetraethylammonium nitrate at 25.0°, as followed by appearance of chloride ion, can be equated to $k_2 k_b / (k_a + k_b)$.

The limiting value of k_2° / α as $\alpha \rightarrow 0$, at high $[AgNO_3]$, will be k_2 . Using the experimental k_2° values, this extrapolated limit was found to be in the region of

(3) H. Burton and P. F. G. Praill, *J. Chem. Soc.*, 729 (1955).

(4) H. Strehlow and H. M. Koepf, *Z. Elektrochem.*, **63**, 373 (1958).

4.8×10^{-4} l. mole⁻¹ sec.⁻¹; a value of 4.77×10^{-4} l. mole⁻¹ sec.⁻¹, taken in conjunction with a value for $k_c/(k_a + k_b)$ of 75 l. mole⁻¹, gives excellent agreement between the calculated and experimental k_2° values.

Table I. Correlation of Calculated and Experimental Second-Order Rate Coefficients, k_2° (l. mole⁻¹ sec.⁻¹), for Reaction of Methyl Chloroformate with Silver Nitrate in Acetonitrile at 25.0°

[AgNO ₃]	α	$10^4 k_2^\circ$, exptl.	$10^4 k_2^\circ/\alpha$	$10^4 k_2^\circ$, calcd.
0.00100	0.94	2.23	2.4	2.06
0.00200	0.89	2.12	2.4	2.08
0.00500	0.79	2.13	2.7	2.08
0.0100	0.69	1.96	2.8	2.03
0.0200	0.57	1.82	3.2	1.87
0.0400	0.45	1.68	3.7	1.62
0.0800	0.35	1.32	3.8	1.36
0.160	0.26	1.08	4.2	1.07

The values for k_2 of 4.77×10^{-4} l. mole⁻¹ sec.⁻¹ and for $k_2 k_b/(k_a + k_b)$ of 2.00×10^{-4} l. mole⁻¹ sec.⁻¹ show that in acetonitrile at 25.0°, and in the absence of any silver ion assistance to chloride ion removal, an intermediate anion has a 0.42 probability of decomposing by loss of chloride ion and a 0.58 probability of decomposing by loss of nitrate ion.

When 0.0100 *M* silver perchlorate was added to a 0.0100 *M* solution of silver nitrate reacting with 0.0935 *M* methyl chloroformate, the integrated k_2° values (based on stoichiometric nitrate ion concentration) fell in value as reaction proceeded; the initial k_2° value was 1.83×10^{-4} l. mole⁻¹ sec.⁻¹. Although the addition of silver perchlorate will increase the partitioning of the intermediate to products, an accompanying reduction in the concentration of dissociated nitrate ion will decrease the rate of formation of the intermediate.

The success of the theoretical analysis can be taken as an excellent additional evidence⁵ for the formation in nucleophilic substitution reactions at carbonyl carbon of an actual intermediate anion, capable of in part reverting to reactants. For suitable replacements of halogen attached to a carbonyl carbon, the treatment allows calculation of the proportions of the intermediate anion which revert to reactants and which go on to give products by loss of halide ion.

Acknowledgment. The authors are grateful to the Petroleum Research Fund of the American Chemical Society for partial support of this work.

(5) (a) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951); (b) for a very recent review, see T. C. Bruice and L. R. Fedor, *ibid.*, **86**, 4886 (1964).

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The Crystal and Molecular Structures of 7-Chloro- and 7-Bromo-4-hydroxytetracycloxide

Sir:

The synthesis of a new class of tetracyclines,¹ called "tetracycloxides," was recently reported.^{2,3} This com-

(1) R. C. Esse and G. M. Sieger, South African Patent Application 63/4791 (filed Oct. 22, 1963, accepted March 25, 1964).

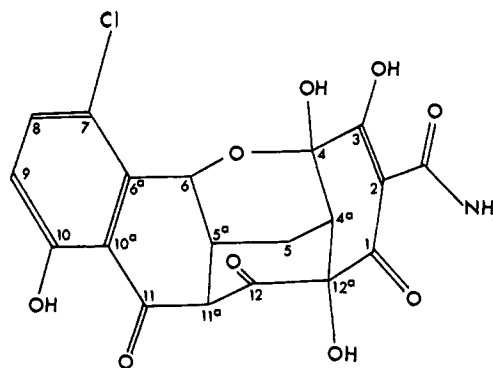


Figure 1. 7-Chloro-4-hydroxytetracycloxide.

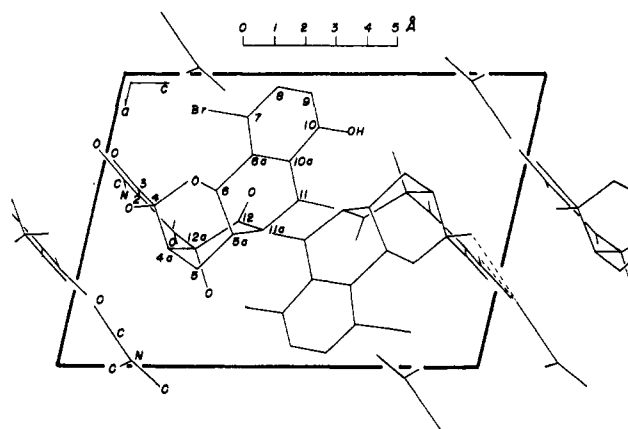


Figure 2. Projection of the unit cell along the *b*-axis.

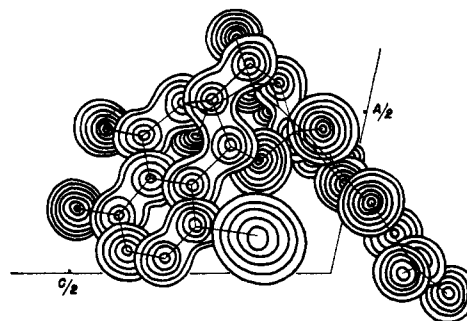


Figure 3. Composite electron density map showing one asymmetric unit: contours at 1 e Å.⁻³ (for bromine, 5 e Å.⁻³), zero contour omitted.

munication represents a preliminary account of the results of the single crystal X-ray analysis of two halogenated tetracycloxides. This work was undertaken to verify unambiguously the proposed structure for these compounds, especially the presence of the C(4)-O-C(6) hemiketal link.

Single crystals of 7-chloro- (I) and 7-bromo-4-hydroxytetracycloxide (II) found to be solvated with dimethylformamide (DMF) were obtained *via* the vapor-phase transfer method using DMF as the solvent and water as the transfer agent. The crystals obtained

(2) R. C. Esse, J. A. Lowery, C. R. Tamorria, and G. M. Sieger, *J. Am. Chem. Soc.*, **86**, 3874 (1964).

(3) R. K. Blackwood and C. R. Stephens, *ibid.*, **86**, 2736 (1964).