simple esters and much work has gone into the investigation of possible synthetic methods.[1] To date the compounds have not been available. We wish to report the synthesis of esters of both the acids by a simple modification of the Claisen ester condensation of ethyl oxalate with α- and γ-picoline.

For reasons which will be given later, it appeared to us that previous attempts failed because of either too great or too little activity of the basic co-reactant used, and a metal derivative of the picolines of somewhat intermediate reactivity seemed to be indicated. If 2-picolyllithium is treated with anhydrous cadmium chloride and the resulting picolylcadium is treated at −70° in ether with ethyl oxalate a 10% yield of easily purified ethyl 2-pyridylpyruvate is obtained as light-yellow crystals melting at 82.5–83.5° (*Anal.* Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.35; H, 5.85; N, 7.18).

Use of cadmium chloride was not effective in the case of 4-picoline but when mercuric chloride was substituted for it, under almost identical conditions, a 10% yield of ethyl 4-picolylpyruvate was obtained. This ester was also easily isolated and purified and appeared as an orange-yellow powder which melted at 138–139°. (*Anal.* Calcd. for $C_{10}H_{11}O_3N$: C, 62.16; H, 5.74; N, 7.25. Found: C, 62.3; H, 5.95; N, 7.08).

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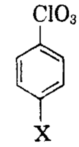
(1) C. R. Hauser and W. J. Humphlett, *J. Am. Chem. Soc.*, **72**, 3805 (1950); R. Adams and S. Miyano, *J. Am. Chem. Soc.*, **76**, 3168 (1954).

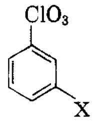
Hydrogenolysis of Perchloryl Aromatic Compounds

Sir:

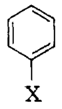
When some representative perchloryl aromatic compounds, I and II, dissolved in glacial acetic acid, were stirred in contact with a palladium-on-charcoal catalyst and with hydrogen,[1] they absorbed the latter rapidly.[2] The products were identified by ultraviolet spectral data as being the deperchlorylated compounds (III). The stoichiometry of the reaction corresponds generally to



I,a. X = H
b. X = F
c. X = OCH_3



II, X = NO_2
X = NH_2



III

$$ArClO_3 + 4H_2 \longrightarrow ArH + HCl + 3H_2O \quad (1)$$

There are two qualifications we must offer to the above statements. First, *m*-nitroperchlorylbenzene absorbed not 4, but 7 moles of hydrogen corresponding to reduction of the nitro-group as well as hydrogenolysis of the perchloryl moiety. Second, our qualitative series of runs revealed no apparent structural influence on rate of hydrogenolysis, the uptake of hydrogen being quite rapid and essentially complete in 30 minutes at room temperature. The only exception was *m*-aminoperchlorylbenzene which as the free base readily underwent reaction (1) but which when placed in solution as its hydrochloride, was resistant to hydrogenolysis. The cause of this anomaly is being examined further.

When 95% ethanol was used as solvent the absorption of hydrogen observed was step-wise, one mole being taken up very rapidly and the other three much more slowly. These data suggest the following sequence for the overall hydrogenolysis (1).

$$ArClO_3 + H_2 \longrightarrow ArH + HClO_3 \quad (2)$$

$$HClO_3 + 3H_2 \longrightarrow HCl + 3H_2O \quad (3)$$

Calibrating experiments with chloric acid solutions in both glacial acetic acid (where reduction is rapid) and 95% ethanol (where reduction is slow) confirm this sequence of cleavage. In a critical experiment, a solution of Ia in 95% ethanol was allowed to take up one molar proportion of hydrogen, it was then filtered, extracted with ether, and the aqueous mother liquor was shown to contain 88% of the calculated chlorate content in accord with equation (2). An alternative mode of scission to the observed initial C—Cl rupture would involve initial Cl—O cleavages (to yield Ar—Cl) followed by its hydrogenolysis. This Ar—Cl intermediate in the case of Ia, *viz.* chlorobenzene was not hydrogenolyzed under our conditions.

These results also have some implication with regard to the structure of compounds of type (I). If the perchloryl compounds had the structure Ar—O—ClO_2 instead of the well established one, $ArClO_3$,[3] then one might anticipate their hydrogenolysis being akin to those of the analogous nitrate esters[4] and they should then proceed as follows:

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(1) These hydrogenolyses were all run at room temperature and on a micro scale. The apparatus, technique, and catalyst used were as described by C. L. Ogg and F. J. Cooper, *Anal. Chem.*, **21**, 1400 (1949).

(2) An earlier probing experiment failed to reveal appreciable reaction between hydrogen with palladium catalyst and perchlorylbenzene [C. E. Inman, R. E. Oesterling, and E. A. Tyczkowski, *J. Am. Chem. Soc.*, **80**, 5286 (1958)]. The present data now amend this erroneous impression. Other than the possibility that the earlier run may have contained some impurities which poisoned the catalyst, and the fact that it was not run on a quantitative scale, we cannot explain the negative result.

(3) See Inman, *et al.*, *J. Am. Chem. Soc.*, **80**, 5286 (1958).

(4) L. P. Kuhn, *J. Am. Chem. Soc.*, **68**, 1761 (1946).

$$ROClO_3 + 3H_2 \longrightarrow ROH + HCl + 2H_2O$$

Neither the observed stoichiometry nor the observed cleavage pattern of the perchloryl compounds conforms to this last equation. The present data thus support our earlier structural conclusions.[3,5]

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(5) Another indication of the difficulty of Cl—O cleavage in the aromatic perchloryl compounds was given by a preliminary attempt at a polarographic assay. With a dropping mercury electrode from 0.0 to −2.0 v., an 0.05 *M* solution of perchloryl benzene in 50% aqueous ethanol with lithium chloride as supporting electrolyte gave no reductive wave in either neutral, weakly acidic or weakly alkaline solution.